CHARACTERISING AND MODELLING URBAN RUNOFF QUALITY FOR IMPROVED STORMWATER MANAGEMENT

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Abstract

Runoff from impermeable urban roof, road and carpark surfaces are key contributors of sediment and heavy metals to urban waterways, causing acute and chronic adverse effects on the aquatic ecosystem. Characterisation of the untreated runoff quality is necessary to guide the selection of effective and efficient stormwater management options that can reduce the pollutant load. Rainfall characteristics, such as intensity, storm duration, rainfall pH and the length of antecedent dry periods, are also known to be key drivers of stormwater pollution build-up and wash-off processes. However, there is limited knowledge of how low intensity rainfall climates, such as is found in Christchurch, New Zealand, influence pollutant generation.

Current stormwater pollutant load models typically aggregate the contributing surface areas by land use or are annual load models that use per area pollutant load factors. While annualised load models are useful in quantifying the cumulative effects of pollutants from stormwater discharges on the receiving environment, storm-event based models are needed to identify the peak concentrations responsible for acute toxicity effects as well as informing design criteria of any stormwater treatment system based on pollutant characteristics. As pollutant build-up and wash-off processes are known to differ for various surface materials, load prediction from an individual surface enables targeting of ‘hotspot’ surfaces and assists with selecting appropriate management options for that particular surface’s characteristics. Thus, the main objective of this research was to characterise pollutant generation in a low intensity rainfall climate from different impermeable urban surface types and then develop an event-based pollutant load model to predict pollutant loads from those different surface type within a catchment. The research therefore had the following elements: (1) characterisation of sediment and heavy metal concentrations in untreated urban runoff from specific impermeable urban surfaces, (2) characterisation of particle size distribution (PSD) variance in the runoff, (3) development of an event-based model for total suspended solids (TSS), copper and zinc event loads using rainfall characteristics as predictor variables, and (4) application of the model to case study catchments.

Untreated runoff samples were collected from 25 rainfall events from four impermeable surfaces (concrete tile, copper, and galvanised roofs and an asphalt road) located within 320 m of each other in a residential/institutional catchment in Christchurch. Pollutant concentrations were found to be significantly different between surfaces, confirming that quantification and prediction of pollutant loads from urban surfaces should take account of the different surface materials. The highest concentrations of TSS were seen in the asphalt road runoff under both initial and steady state conditions. As the road TSS was substantially higher than roof TSS, treatment of road runoff prior to it mixing in the kerb and channel with roof runoff may be warranted to reduce the ‘treatable’ volume for TSS.

Substantial PSD variation was observed for each surface and between events, particularly for coarser road and concrete roof surfaces. Implications of this variation result in a wide range in predicted treatment performance since most sediment treatment is dependent on particle size and retention time.

This suggests that short-retention treatment devices carry a high performance risk of not being able to achieve adequate TSS removal across all rain events.

Copper and galvanised roof runoff had the highest copper and zinc concentrations, respectively, followed by road runoff. The majority of the copper in the copper roof runoff was in dissolved form (average of 77%), while only 28% of the road runoff copper was dissolved. Likewise, almost all (average of 99%) the zinc in the galvanised roof runoff was in dissolved form, while only 42% was dissolved in road runoff. As well as contributing to ecotoxicity in the receiving environment, dissolved metals in stormwater runoff can be more difficult to treat as majority of the standard stormwater treatment systems are based on filtration or settling processes that primarily aim to remove sediment. Therefore, source reduction of roof-contributed copper and zinc should be targeted via roof material replacement or painting. Road runoff treatment systems should consider processes that facilitate both dissolved and particulate metals, as removal of particulate-associated metals via settling or filtration may not adequately reduce metals loads entering urban waterways.

The event-based pollutant load model, Modelled Estimates of Discharges for Urban Stormwater Assessments (MEDUSA), developed as part of this research, was found to be effective at modelling TSS, and total and dissolved copper and zinc loads under a low intensity rainfall climate. MEDUSA was calibrated against observed data and applied to two case study catchments in Christchurch, New Zealand. The model clearly identified the spatial distribution of pollutant generation across each catchment's individual roof, road and carpark surfaces, and was found to be most sensitive on an event-to-event basis to rainfall intensity and duration, both factors which are expected to change under future climate change scenarios for Christchurch. The MEDUSA model can be further used to explore the effectiveness of different management scenarios on reducing pollutant loads and also employed for guiding the prioritization, location and selection of stormwater treatment systems to ultimately improve urban waterway health through reduction of untreated stormwater-generated pollutants. Enhancements to the MEDUSA framework can be advanced by incorporating other pollutants of concern, such as nutrients, emerging contaminants and other metals of concern.

Overall, this research contributes to scientific understanding of both at-source stormwater character and the effectiveness of using rainfall characteristics to predict pollutant loads based on simulating build-up and wash-off processes. Specifically, the research has identified how urban surface types differ in their pollutant generation, (i.e. the relative influence of rainfall and material characteristics in generation of both sediment and metal pollutants); how heavy metals partition between particulate and dissolved state in untreated runoff from different urban surfaces (with implications for metals treatment selection); how particle size fractionation differs during and between rain events from different urban surfaces (with implications for sediment treatment system performance); and the importance and effectiveness of using a disaggregated model (i.e. individual surface-based modelling) as the pollutant generation processes differ significantly between different urban surface types.

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Charters, F., Cochrane, T. A. and O'Sullivan, A. (2015). Particle size distribution variance in untreated urban runoff and its implication on treatment. *Water Research,* 85, 337-345.

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Fraga, I., Charters, F., O'Sullivan, A., and Cochrane, T. (2016). A novel modelling framework to prioritize estimation of non-point source pollution parameters for quantifying pollutant origin and discharge in urban catchments. *Journal of Environmental Management*, 167, 75-84.

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Name: *Tom Cochrane* Signature: Date: *27 April 2016*

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Table of Contents

List of Tables

List of Figures

Abbreviations and Acronyms

ADD	Antecedent dry days
Al	Aluminium
ANZECC	Australian and New Zealand Environment and Conservation Council
ARMCANZ	Agricultural and Resource Management Council of Australia and New Zealand
As	Arsenic
CCC	Christchurch City Council, the local territorial authority
Cd	Cadmium
Co	Cobalt
COD	Chemical oxygen demand
Cr	Chromium
Cu	Copper
DEPTHp	Depth of preceding rain event (mm)
DEPTHt	Depth of current rain event (mm)
DRP	Dissolved reactive phosphorus
DUR	Duration of rain event (hours)
EMC	Event mean concentration
Fe	Iron
GIS	Geographic Information Systems
ICP-MS	Inductively coupled plasma mass spectrometry
INTavg	Average rainfall intensity (mm/hr)
INTpk	Peak (5-min) rainfall intensity (mm/hr)
IQR	Interquartile range
LWRP	Land and Water Regional Plan
MEDUSA	Modelled Estimates of Discharges for Urban Stormwater Assessment
Mn	Manganese
MUSIC	Model for Urban Stormwater Improvement Conceptualisation
Ni	Nickel
NIWA	National Institute of Water and Atmospheric Research
NPDES	National Pollutant Discharge Elimination System
NSE	Nash Sutcliffe Efficiency
NZTA	New Zealand Transport Authority
Pb	Lead
PBIAS	Percent Bias
PSD	Particle size distribution

R	A statistical modelling package
SS	Steady state
SWMM	Storm Water Management Model
TSS	Total suspended solids
USEPA	United States Environmental Protection Agency
V	Vanadium
WQ	Water quality
Zn	Zinc

Research Outputs

Journal Papers

1. Charters, F., Cochrane, T. A. and O'Sullivan, A. (2016). Predicting sediment and heavy metal event loads from roof and road surfaces, In draft, *Environmental Modelling and Software*.

2. Charters, F., Cochrane, T. A. and O'Sullivan, A. (2016). Untreated runoff quality from roof and road surfaces in a low intensity rainfall climate, *Science of the Total Environment,* 550, 265-272.

3. Fraga, I., Charters, F., O'Sullivan, A., and Cochrane, T. (2016). A novel modelling framework to prioritize estimation of non-point source pollution parameters for quantifying pollutant origin and discharge in urban catchments*. Journal of Environmental Management*, 167, 75-84.

4. Charters, F., Cochrane, T. A. and O'Sullivan, A. (2015). Particle size distribution variance in untreated urban runoff and its implication on treatment. *Water Research,* 85, 337-345.

Peer-reviewed Conference Proceedings

1. Charters, F., Cochrane, T. A. and O'Sullivan, A. (2016). Characterising urban zinc generation to identify surface pollutant hotspots in a low intensity rainfall climate. In: International Water Association World Water Congress, 9-14 October 2016, Brisbane, Australia, 8pp.

2. .Charters, F., Cochrane, T. A. and O'Sullivan, A. (2016). Predicting event-based stormwater contaminant loads from individual urban surfaces. In: Water New Zealand 2016 Stormwater Conference Proceedings, 18-20 May 2016, Nelson, New Zealand, 14pp.

3. Charters, F., Cochrane, T. A. and O'Sullivan, A. (2014). Modelling stormwater contaminant loads in older urban catchments: Effects of climate influences on selecting management options, In: International Water Association 13th International Conference on Urban Drainage Proceedings, 7-12 September 2014, Kuching, Malaysia, 8pp.

4. Charters, F., Cochrane, T. A. and O'Sullivan, A. (2014). Modelling stormwater management options for enhancing water quality of urban streams. In: Water New Zealand 2014 Stormwater Conference Proceedings, 14-16 May 2014, Christchurch, New Zealand, 12pp.

Conference Abstracts (Oral Presentations)

1. Charters, F., Cochrane, T. A. and O'Sullivan, A (2016). Modelling sediment and heavy metal loads in stormwater from different impermeable urban surfaces. Water New Zealand Modelling Symposium, 16-17 March 2016, Wellington, New Zealand.

2. Charters, F., Cochrane, T. A. and O'Sullivan, A. (2015). Predicting stormwater pollution from urban surfaces in Christchurch. Waterways Postgraduate Conference, 17 November 2015, Christchurch, New Zealand.

3. Charters, F., Cochrane, T. A. and O'Sullivan, A. (2015). Characterizing urban runoff particle size distributions and the implications for stormwater treatment. World Environmental and Water Resources Congress 2015, 17-22 May 2015, Austin, US.

4. Charters, F., Cochrane, T. A. and O'Sullivan, A. (2014). Particle size analysis of runoff from impermeable surfaces. 2014 Water Symposium, 24-28 November 2014, Blenheim, New Zealand.

5. Charters, F., Cochrane, T. A. and O'Sullivan, A. (2014). Characterising untreated urban runoff quality in Christchurch. Waterways Postgraduate Conference, 18 November 2014, Christchurch, New Zealand.

6. Charters, F., O'Sullivan, A. and Cochrane, T. A. (2013). Stormwater quality modelling to improve water quality of urban waterways. Waterways Postgraduate Conference, 12 November 2013, Christchurch, New Zealand.

1 Introduction

1.1 Statement of problem

Stormwater runoff from impermeable urban surfaces during rain is recognised globally as a key polluter of urban waterways (Hvitved-Jacobsen *et al.* 2010). In many urban areas, untreated runoff is discharged directly into the nearest waterway, causing various adverse impacts on the aquatic ecosystem (Marshall *et al.* 2010; Barbosa *et al.* 2012). Previous urban instream water quality studies in New Zealand (Auckland Regional Council 1992a; Zanders 2005; Brown & Peake 2006; Auckland Regional Council 2010b; Marshall *et al.* 2010), for example, have identified sediment, copper, zinc and lead as pollutants of most concern in urban waterways. The quality of stormwater reaching the waterway can be improved through both pollutant source reduction measures and treatment measures; however, it is critical to understand the untreated stormwater quality to guide the selection of appropriate stormwater management measures.

Pollutant build-up and wash-off differs between impermeable surface types, as these processes are influenced by factors such as surface material type, condition, age, orientation and traffic presence. Total suspended solids is contributed to urban surfaces via atmospheric deposition of particles (dry and wet deposition), breakdown and degradation of surface materials and direct deposition from vehicular sources (e.g. tyre and brake pad wear, dust wash off from vehicle bodies) (Zanders 2005). Copper (Cu) is contributed from brake pads (it is used as a heat dissipater), industrial uses of Cu (released into the airshed and settled with atmospherically deposited particles) and direct dissolution of Cu materials (such as roofing or air conditioning piping) (Davis *et al.* 2001; O'Sullivan *et al.* 2012; Wicke *et al.* 2012b). Zinc (Zn) is contributed from tyres (it is used as a vulcanising agent in tyre rubber), industrial uses of Zn and direct dissolution of Zn materials, such as galvanised roof cladding. Lead (Pb) has historically been contributed to urban runoff from accumulated past usage of leaded fuels in soils, old paint, as well as from current contributions from vehicles' tyre weights (Kayhanian 2012; Egodawatta *et al.* 2013).

The build-up and wash-off processes of pollutants from impermeable surfaces are driven by rainfall characteristics such as intensity, rainfall pH, number of antecedent dry days and event duration. While the physical pollutant processes are universal, rainfall characteristics differ across climate zones and therefore pollutant generation in any given catchment is dependent upon the local climate. Christchurch, New Zealand, provides an example of a low intensity rainfall climate, whereas most previous international untreated runoff characterisation studies have been in higher intensity rainfall climates. The adverse effects of stormwater pollutants are still observed in local waterways despite the low rainfall intensities and therefore characterisation is needed of the relationship between different surface types and pollutant loads both during individual rain events and across multiple events in a low intensity climate.

The particle size distribution (PSD) of the sediment being generated from impermeable urban surfaces has also had limited study. The PSD of the sediment in the runoff dictates the sediment removal efficiency of physical-based settling and filtration treatment systems used to reduce the sediment load that reaches the receiving waterway, as the PSD controls sediment settling rates. Therefore, if effective sediment removal is to be achieved through such systems, the variation of the PSD of the sediment needs to be better understood to ensure appropriate treatment system selection and design.

While best practice stormwater management systems, such as swales, stormwater detention ponds and wetlands are readily implemented in new greenfield developments to reduce pollutant loads prior to discharge into the receiving environment, it is more difficult to retrofit them into established urban areas where water quality was rarely considered during urbanisation. This difficulty comes from having more site constraints, including space limitations, existing land use activities, and integration with existing infrastructure and the existing urban landscape. All these factors need to be considered in the planning and design of stormwater retrofits, as they influence their feasibility, cost and performance. Treatment selection is also influenced by factors such as heavy metal partitioning (i.e. the amount of metals in particulate or dissolved form) as the partitioning form controls the processes that are likely to be effective at removing metals from specific runoff. Particulate metals can be removed via physical settling and filtration, while removal of dissolved metals requires more complex treatment involving precipitation, sorption, filtration, uptake and/or binding. Therefore, any characterisation of heavy metals in runoff quality should include partitioning between dissolved and particulate forms.

The characterisation of untreated runoff in relation to different impermeable surface types and local rainfall characteristics can then be used to develop a predictive model for estimating the pollutant load being generated from each surface under a range of rainfall conditions. These models can assist with the development of targeted stormwater management strategies. However, current models have typically focused on predicting annual loads across a whole catchment. Annual load models typically aggregate the contributing surface areas and apply unit area pollutant load factors to estimate the annual load for each pollutant. They are therefore valuable for assessing the potential toxicity and cumulative effects of pollutants from stormwater on the receiving environment but are limited in their ability to guide strategies for reducing stormwater pollution at or near source. Conversely, event-based models can predict the amount of pollutant generated by a single rain event and can guide selection of appropriate management options (e.g. source reduction or engineered treatment systems) to reduce pollutant loads prior to discharge into the environment. Furthermore, modelling individual surfaces' contributions to pollutant loads, rather than aggregating by land use or catchment, enables identification of 'hotspot' surfaces that should be targeted for efficient stormwater management and informs where stormwater treatment could be best located within a catchment.

1.2 Research objectives

The main objectives of this research were to characterise pollution generation in a low intensity rainfall climate from different impermeable urban surface types and also develop an event-based pollutant load model to predict pollutant loads from those surfaces within a catchment. The research therefore had the following elements: (1) characterisation of sediment and heavy metal concentrations in untreated urban runoff from specific impermeable urban surfaces; (2) characterisation of particle size distribution (PSD) variance in the runoff; (3) development of an event-based model for total suspended solids (TSS), copper and zinc event loads using rainfall characteristics as predictor variables; and (4) application of the model to case study catchments.

Characterisation of sediment and heavy metal concentrations: the objectives of this component were to identify how much pollution is being generated from individual impermeable surfaces and assess whether there are significant differences in pollutant loads from different surface types (where the surfaces are within the same catchment). Heavy metal concentrations were also characterised in terms of particulate and dissolved partitioning as this is crucial information for selection of an appropriate treatment approach.

Characterisation of PSD variance: the objectives of this component were to assess whether there was significant intra- and inter-event variation in PSD in the runoff. This research aspect also aimed to characterise typical PSD profiles for each impermeable surface type, assess whether differences between surfaces were significant and conclude whether key PSD metrics (such as median particle diameter) were related to rainfall characteristics in a low intensity climate. Similarly to the metals partitioning characterisation, the PSD characterisation was motivated by the need to better understand particle size fractionation to inform selection of appropriate sediment removal systems.

Development of model framework: the model development stage focussed on developing an event-based pollutant load model, using rainfall characteristics as predictor variables to adequately describe generic pollutant build-up and wash-off processes that could be applied to any catchment in any climate once model coefficients were calibrated for the local rainfall conditions.

Application of model to case study catchments: the application of the model to case study catchments had two objectives: 1) evaluation of how the modelling results could be used to better understand pollutant load distribution in a catchment and subsequently utilise the results to inform stormwater management decision-making; and 2) evaluation of the sampling and recalibration process required to reapply the model to a new catchment.

To address these research objectives, untreated runoff samples were collected from 25 rainfall events over all seasons from four impermeable surfaces (concrete tile, copper, and galvanised roofs and an asphalt road). The sampling sites were located within 320 m of each other in a residential/institutional catchment in Christchurch. The samples were analysed for TSS, total and dissolved copper, lead and zinc, PSD and alkalinity (where relevant). A model framework was concurrently developed to predict TSS, total and dissolved copper and zinc build-up and wash-off from roof, road and carpark surfaces. The model was then calibrated using the sampled dataset. A second, limited period of runoff sampling (9 events from 7 surfaces over two seasons) was undertaken in the second case study catchment and the model was recalibrated and run for this new catchment.

1.3 Thesis structure

Chapters 1 through 3 provide background and framework to the techniques used in this research. The results Chapters, 4 through 7, are structured with a brief summary of relevant background knowledge and principally comprise an analysis of the data presented in each results chapter.

Chapter 1: Introduction	The need for and scope of this research
Chapter 2: Literature Review	Background knowledge of untreated runoff characteristics and stormwater quality modelling techniques that give context to this research.
Chapter 3: Methodology	Field sampling techniques, laboratory analysis techniques, rainfall characterisation, statistical analyses, model development and calibration techniques.
Chapter 4: Sediment and Heavy Metal Characteristics of Untreated Runoff	Pollutant ranges for each impermeable surface type and comparison between surfaces, assessment of first flush presence, relationships between total and dissolved metals, and comparison of this study's observations with internationally reported data. Linking pollutant sources with wash-off behaviour, implications for approaches to pollutant modelling.
Chapter 5: Particle Size Distribution of Untreated Urban Runoff	Typical PSD profiles for each surface type, intra-event variation, inter-event variation, comparison between surfaces, relationships between key PSD metrics and rainfall characteristics, putting observed PSD in context with international observations.
Chapter 6: Development and Application of Pollutant Load Modelling Framework	Outline of new pollutant load framework (MEDUSA: Modelled Estimates of Discharges for Urban Stormwater Assessments) including mathematical relationships used within model. Calibration process and assessment of model performance. Application of MEDUSA to an initial case study catchment.
Chapter 7: Pollutant Load Model Applications – Addington Brook Catchment	Recalibration process and application of MEDUSA to a second case study catchment.

2 Literature Review

2.1 Overview

This chapter gives context to this research by providing background information on the character and effects of stormwater pollutants (Sections 2.2); the legislative environment that mandates improved stormwater management (Section 2.3); stormwater management options, the challenge of retrofitting and the state of current practice in Christchurch (Section 2.4); and an overview of stormwater pollutant load modelling techniques, existing models and their limitations (Section 2.5).

2.2 Stormwater pollutants: their characteristics and effects on the receiving environment

2.2.1 Overview

Urban runoff contributes a wide range of pollutants into waterways, including sediment, heavy metals, nutrients, pathogens and organics such as hydrocarbons and synthetic polymers (Rossi *et al.* 2005). These pollutants are derived and entrained in runoff via processes of atmospheric deposition, material degradation, dissolution and erosion (Zanders 2005; Egodawatta *et al.* 2009; Wicke *et al.* 2012a). Table 2-1 summarises the anthropogenic sources of pollutants expected to be found in urban stormwater.

Table 2-1: Anthropogenic sources of pollutants in discharges to urban waterways (Sansalone & Buchberger 1997b; Waters 2011; Wicke *et al.* 2012a)

Source	Associated activity	Solids	Heavy metals [1]	Aromatic organics	Nutrients [2]	Surfactants
Vehicle brakes	Degradation in use		Cd, Cu, Pb, Zn			
Vehicle tyres	Degradation in use		Cd, Cr, Cu, Fe, Ni, Pb, Zn			
Vehicle frame and body	Car washing, rain wash off	✓	Fe, Zn			
Fuels, oils, grease	Industrial sites, vehicles		Pb, Vd, Zn			
Fuel combustion	Vehicle emissions, domestic fires			✓		
Concrete pavement	Degradation over time	✓				
Asphalt pavement, including coal-tar material	Degradation over time	✓		✓		
Litter (gross pollutants)	Various	✓	Fe			
Copper piping	Air-conditioning discharges, copper spouting, plumbing		Cu			
Roofing materials (sheet metals, building compounds)	Degradation over time		Cu, Zn			
Paints	Degradation over time		Pb, Zn			
Unvegetated soils	Construction sites, hill catchments	✓				
Household chemicals	Car washing				N, P	✓
Fertilisers	Lawn and garden application with rain wash off				N, P	

[1] Cd: cadmium, Cr: chromium, Cu: copper, Fe: iron, Ni: nickel, Pb: lead, V: vanadium, Zn: zinc

[2] N: nitrogen forms, P: phosphorus

2.2.2 Sediment: Suspended solids

In the urban stormwater context, suspended sediment comprises particulate inorganic or organic matter that is suspended and transported by rainfall-runoff. The finer fraction (<63 µm, i.e. silt and clay) may remain in suspension even at low velocities (low energy environments). Coarser fractions can be initially entrained by rainfall-runoff where energy is high due to sufficient rain intensity and low permeability surfaces, however they may settle out of the water upon entering the receiving waterway (Davies-Colley & Smith 2001).

Sediment is considered a dominant stressor in urban aquatic ecosystems (Marshall et al., 2010) and may cause a wide range of adverse effects on the receiving environment. Excess suspended sediment causes depositional effects such as clogging of the waterway bed (leading to refugia loss and reduction in the exchange capacity between benthic and water column zones), reduced food quality and smothering of biota. There are also suspended effects from sediment discharges such as respiratory damage to aquatic macroinvertebrates, light attenuation and transport of other pollutants such as particulate heavy metals (Ryan 1991; Clapcott *et al.* 2011).

Sediment in urban runoff is heterogeneous in composition as it is derived from several sources. These include direct (local) sources such as vehicle tyre and brake wear, surface material degradation and soil erosion (Zanders 2005; Egodawatta *et al.* 2009; Wicke *et al.* 2012a, b), and indirect (global) sources such as atmospheric deposition (Murphy *et al.* 2014). Nationally and internationally reported mean TSS concentrations show variations between different urban surfaces (Figure 2-1; refer to Appendix A for data sources), reflecting the variation in sediment sources for each surface type). New Zealand studies generally reported lower mean TSS than for equivalent surface types overseas. This is likely caused by factors such as lower concentrations of particulate matter in the atmosphere, lower traffic density and a less intensive industrial history compared to other parts of the world, including North America, East Asia and Europe.

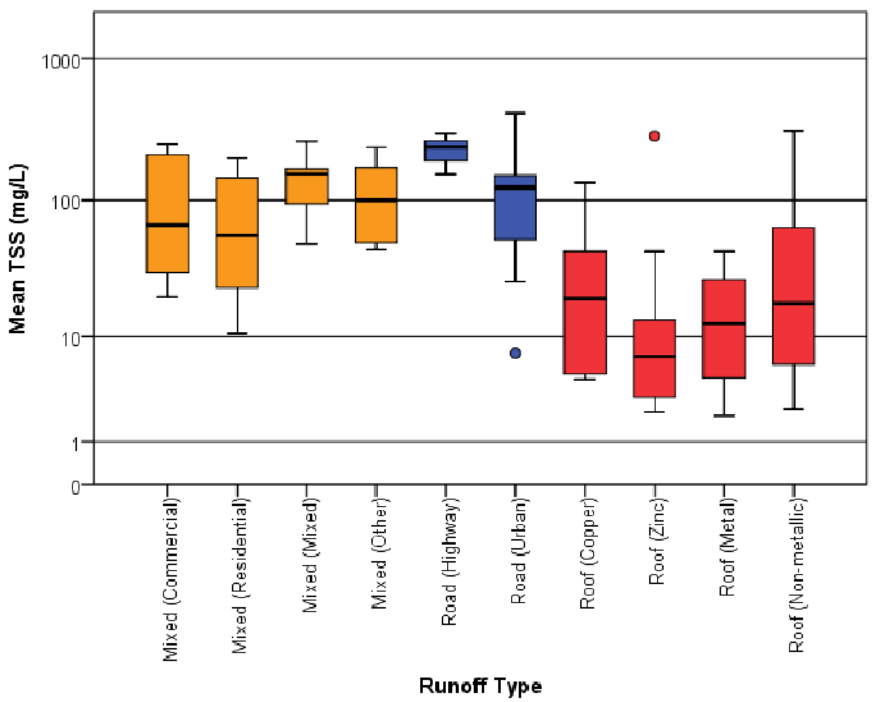


Figure 2-1: Range of internationally reported mean TSS concentrations (mg/L) for different runoff types (◦ denotes outliers ± 1.5 x interquartile range (IQR); refer to Appendix A for data sources)

2.2.3 Sediment: Particle size distribution

The particle size distribution (PSD) of sediment describes the relative amount of particles in each size fraction. Along with individual particle shape, size and composition (i.e. organic or mineral), the overall PSD dictates many of the sediment properties and response to treatment processes and is therefore an important metric in characterising urban runoff quality.

The composition of particle sizes within runoff influences how runoff entrains and transports pollutants and also influences its impact on the receiving environment. Pollutants in stormwater are present in either particulate (>1 μm), colloidal (particles between 1 nm and 1 μm) or dissolved forms. Larger particles (i.e. in the particulate form) can readily settle on beds of waterways, smothering habitat, blocking light, and damaging fish gills and filter-feeders' feeding apparatus. Organisms and plants can absorb pollutants in dissolved form and so this phase is important in terms of ecotoxicity levels.

The particle size composition of stormwater also has implications on effectiveness of different treatment systems. Larger particles can be removed readily via settling in extended detention systems or via physical filtering. However, finer particles may pass untreated through such a system, with colloids requiring, for example, flocculation and coagulation to enhance their settleability before they can be effectively filtered.

Since particles in stormwater runoff come from a wide variety of sources (Table 2-1), it is expected that different impervious surface types will have different particle size distributions (PSDs). Studies of the diversity in particle size composition for untreated runoff are limited and the majority of PSD profiling of runoff to date has focused on road runoff (both highway and urban streets) (Sartor & Boyd 1972; Shaheen 1975; Sansalone *et al.* 1998; Kim & Sansalone 2008), however there is also limited information on mixed source urban runoff. Studies such as Selbig (2013) show large differences in PSDs amongst and between various land uses and urban source areas, confirming that assuming a single PSD profile for a land use type or whole catchment is not likely to be very representative of runoff at any point within the catchment. Overall, road runoff PSDs characteristically show more sediment in the smaller fractions than mixed use or residential data. Furthermore, the PSD in stormwater runoff for any particular event has been found to be related to the rainfall intensity, as the amount of energy available determines the maximum size of particle that can be mobilised during a rain event (DeGroot & Weiss 2008). Understanding the different PSD profiles of individual surfaces within a catchment can be used in models to predict the PSD of runoff from specific surfaces within a catchment. This could greatly assist stormwater managers to develop targeted management plans for high sediment runoff points.

While sediments are pollutants in themselves, they also entrain and transport heavy metals, due to the particles' surface charges binding metals to the particle surface. Heavy metal concentrations have been found to be inversely related to particle size (Sansalone & Buchberger 1997a; Karlsson & Viklander 2008; Selbig 2013) because of the increase in surface charge with decreasing particle size. Therefore, the highest sorbed metal concentration is being contributed by the finer fractions, and it is important this is considered in treatment design decisions. Several studies have reported a trend of increasing copper and zinc concentrations for decreasing particle size fractions for road sediments and rainfall-runoff (Sansalone & Buchberger 1997a; Lau & Stenstrom 2001; German & Svensson 2002; Gunawardana *et al.* 2014). However, there is less variation in lead concentrations across particle sizes (Sansalone & Buchberger 1997a; Zanders 2005). Highway runoff and street sweeping samples (collected via vacuum) generally show higher concentrations in the same particle size range for all three metals compared to lesser-trafficked urban roads.

2.2.4 Copper, lead and zinc in stormwater runoff

Overview

The most commonly detected metals in stormwater runoff are zinc (Zn), copper (Cu), lead (Pb), chromium (Cr), nickel (Ni) and aluminium (Al) (Aryal *et al.* 2010). However, previous instream water quality studies in the Christchurch catchments and elsewhere in New Zealand (Auckland Regional Council 1992a; Zanders 2005; Brown & Peake 2006; Auckland Regional Council 2010b) have identified copper, zinc and lead as pollutants of most concern in urban waterways, and therefore this thesis focuses on these three heavy metals.

Zn is sourced from both roads and zinc-based roofing materials. Galvanised roofing is common in Christchurch, particularly for industrial buildings, contributing zinc through dissolution and degradation. Zn is used as a vulcanising agent in tyre rubber and in brake linings and therefore is contributed to runoff through degradation and wear of these materials. Cu is sourced from copper roofing and cladding material through dissolution, as well as from degradation of car brake linings. Pb has been observed to be declining in the environment since the phasing out of leaded fuels (Kayhanian 2012), however it is still considered to be contributed to urban runoff from accumulated past usage of leaded fuels in soils, old paint, as well as from current contributions from vehicles' tyre weights (Kayhanian 2012; Egodawatta *et al.* 2013).

Copper

Copper (Cu) is naturally occurring in the aquatic environment at concentrations ranging from 0.2 to 30 µg/L (Bowen 1985), derived from natural processes of soil breakdown, decaying vegetation and wildfires. It is an essential element to the vast majority of plant and animal organisms.

However, Cu becomes toxic at elevated levels both to aquatic flora and fauna, as well as to humans. Urban runoff is widely acknowledged as a key contributor of elevated Cu. Its acute toxic effects for aquatic ecosystems include mortality of organisms. Chronic toxic effects include mortality, reduced reproduction rates and reduced organism growth. Adverse effects on public health associated with stormwater-contributed copper may occur through consumption of shellfish that are high in accumulated copper.

Stormwater-derived copper originates from a wide variety of sources across the urban landscape. Industrial uses of copper include electrical wiring, plumbing and air conditioning pipework (Michels *et al.* 2002). Copper is also used in architectural materials such as roofing, flashing, gutters and facades (Perkins *et al.* 2005). Vehicles contribute copper to runoff from abrasion of brake pad linings and from fluid leakage (Boulanger & Nikolaidis 2003). From the mid-1990s, copper fluxes in urban stormwater runoff have been increasing in response to greater urban development (Wallinder & Leygraf 1997;

Landner & Reuther 2004). Figure 2-2 shows the total copper concentrations reported in different urban runoff types (refer to Appendix A for data sources). Copper roofs stand out as consistently having the highest concentration, at least an order of magnitude higher than other categories. Mixed-material and non-zinc roofs also showed elevated copper concentrations, likely due to the use of copper materials in associated fixtures and fittings. Highway runoff was noticeably higher in total copper than runoff from smaller urban roads, while mixed runoff (i.e. runoff mixed from several different surfaces) was similar to urban roads.

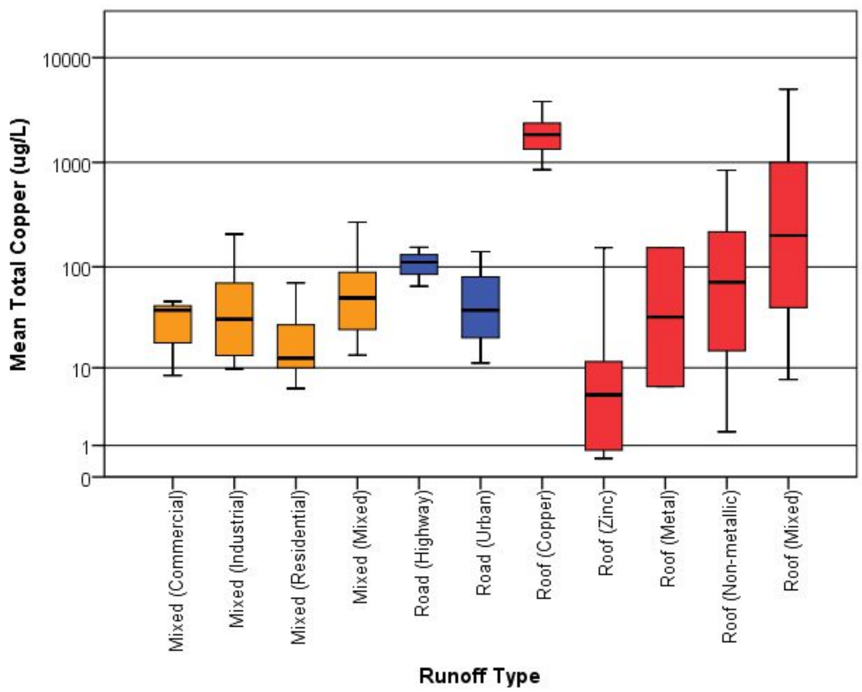


Figure 2-2: Range of internationally reported mean total copper concentrations (µg/L) for different runoff types (showing interquartile range (IQR); refer to Appendix A for data sources)

The ecotoxicological effects of copper are dependent on their form (i.e. dissolved or particulate). Dissolved copper is primarily associated with acute and chronic toxicity effects as this is the form by which organisms can readily uptake copper. Some impermeable surfaces such as copper roofs contribute mostly dissolved copper, while other surfaces such as road surfaces contribute primarily particulate copper (Figure 2-3).

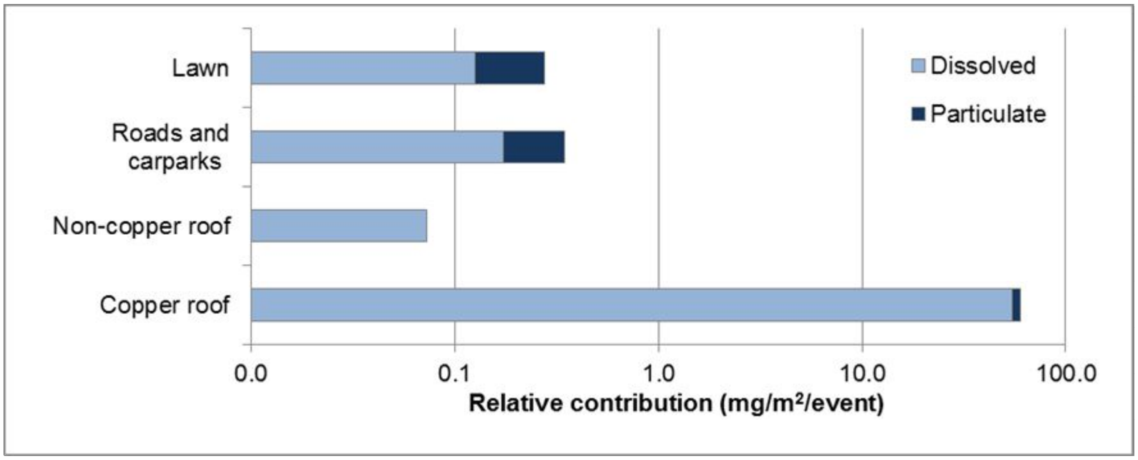


Figure 2-3: Sources and their relative contribution of total and dissolved copper in urban runoff from a 88 ha residential catchment (Data source: Boulanger and Nikolaidis (2003))

Where copper is used on exterior surfaces, natural weathering of the surface (in the presence of oxygen, water, carbon dioxide and/or sulphur-bearing compounds) leads to formation of a patina coating comprised of various compounds including copper oxides, carbonates and sulfates (He *et al.* 2001). Copper dissolution from roof materials can be affected by the age of the surface, as the copper patina itself has been observed to limit the copper concentration leaching into the runoff (Odnevall Wallinder & Leygraf 1997).

Interactions have been observed between copper and other building materials in the course of rainfall runoff and conveyance, which result in removal of the copper ions from the runoff (Boulanger & Nikolaidis 2003). Copper cementation is a precipitation process in which copper ions precipitate onto solid iron surfaces spontaneously. Copper cementation to iron surfaces has been observed by Cantrell *et al.* (1995), and Shokes and Möller (1999) to be an effective mechanism for removing high levels of copper over short time periods. In concrete pipes, copper ions may also bind with available oxygen to form an insoluble oxide, hydroxide or carbonate.

During transportation of copper in runoff between the source and receiving environment (e.g. an urban waterway), the form of copper can also change in response to the assimilation capacity of other substances (e.g. organic materials) that are entrained in the runoff. These substances can bind, complex and sequester the copper, and therefore reduce the amount of bioavailable copper that enters the receiving environment (Perkins et al., 2005). A study by Michels *et al.* (2002) on the acute toxicological effects of copper in an urban waterway from copper roof runoff found that no acute copper toxicity was exhibited at the point of discharge into the stream despite it exhibiting acute copper toxicity at the point of discharge from the roof downpipe. Mixing and binding processes such as dilution, binding with dissolved organic carbons and other complexing agents reduced the amount of copper that was in ionic form before it reached the stream.

Perkins et al. (2005) assessed the effects of various stormwater pipe materials on the concentration of copper, using synthetic stormwater spiked with an average copper concentration of 2,391 µg/L. They found PVC and cast iron pipes had little effect, while the alkalinity of the concrete pipes resulted in significant removal of ionic copper (and total and dissolved copper, as ionic copper was the predominant copper form) over short distances (within 1 metre). Once absorbed, the copper did not readily leach from the runoff in the concrete pipe when subsequently mixed with copper-free water. They recommended that concrete pipes be considered as an option to remove copper from stormwater, either as the stormwater pipe material of choice or within a stormwater treatment filtration system (Good *et al.* 2014). This finding also suggests that where concrete tile roof water is mixed with runoff from higher copper-contributing sources such as copper roofs and roads, the remnant alkalinity in the concrete roof runoff will assist in reducing the copper toxicity of the runoff.

Zinc

Like copper, low levels of zinc (Zn) also naturally occur in the aquatic environment due to weathering of minerals (Novotny 1995). Elevated levels can bioaccumulate in organisms and be carried up the food chain. Algae, crustaceans and salmonids are particularly sensitive to elevated zinc levels. Public health concerns associated with zinc in the aquatic environment focus largely around consumption of shellfish that have accumulated zinc while filter-feeding. For example, in Christchurch City, the regional council recommend against collecting shellfish within the Estuary of the Heathcote and Avon Rivers/Ihutai due to elevated heavy metals, including Zn, in the estuarine sediments.

Zinc can be contributed to stormwater from roof surfaces, including from galvanised steel and Zincalume® sheeting. Zinc release can occur as the result of direct dissolution of the material during rainfall. Rainfall pH is typically, albeit mildly, acidic due to the entrainment of CO_2 from the atmosphere as the raindrops fall (i.e. forming carbonic acid when mixed with water). Some corrosion can also occur during dry periods, as sulphur oxides (SO_x) and nitrous oxides (NO_x) settle on the surface enhancing the acidity, with the corroded surface then releasing zinc during rain. Vehicles also contribute zinc as it is a vulcanizing agent in tyre rubber, and is therefore contained in the tyre wear particles that are deposited on the road surfaces. Figure 2-4 summarises the reported total zinc concentrations from international and New Zealand literature (refer to Appendix A for data sources), with zinc roof runoff showing the highest reported mean concentration.

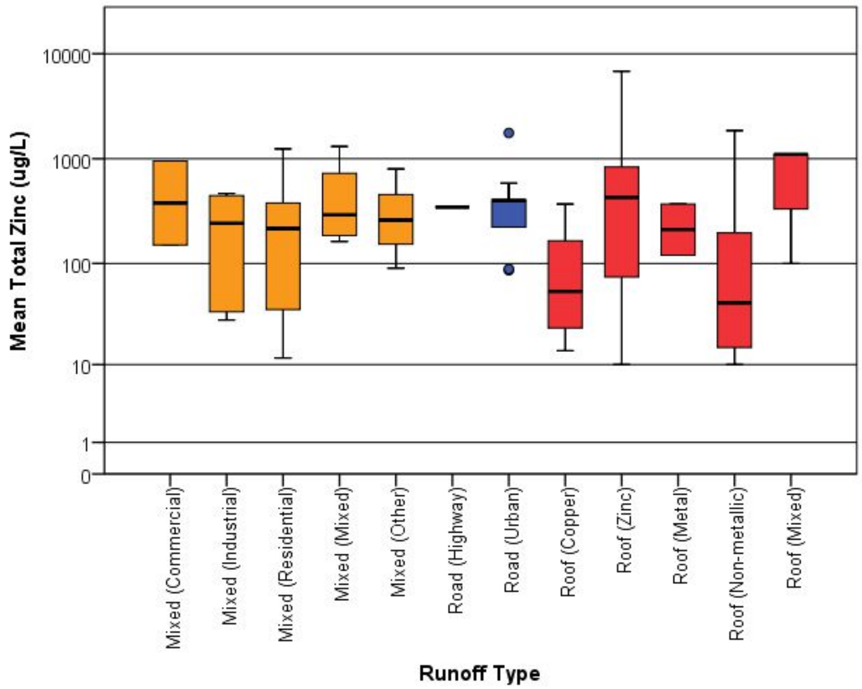


Figure 2-4: Range of internationally reported mean total zinc concentrations (µg/L) for different runoff types (◦ denotes outliers ± 1.5 x interquartile range (IQR); refer to Appendix A for data sources)

Lead

Historically the use of lead (Pb) has been widespread due to its ductility and low corrosiveness (Förstner & Wittmann 2012), although its toxicity to humans and aquatic organisms has also been long recognised. Excess Pb in humans affects the brain, central nervous system, and is also associated with chronic kidney disease. Aquatic organisms can rapidly take up organic lead from water and sediment, as well as more slowly take up particulate-bound inorganic lead.

Pb has been observed to be declining in the environment since the phasing out of leaded fuels (Kayhanian 2012; Huber *et al.* 2016). There are now many restrictions on allowable lead levels in paints; for example, the New Zealand Transport Authority (NZTA) sets a limit of 140 ppm lead in roadmarking paints (NZTA 2009). Pb is still considered to be contributed to urban runoff from accumulated past usage of leaded fuels in soils, old paint, as well as from current contributions from vehicles' tyre weights (Kayhanian 2012; Egodawatta *et al.* 2013).

Heavy metals partitioning

Heavy metals are known ecotoxicants in the aquatic environment (Mance 1987; Harding 2005). Their behaviour and toxicity are determined by the metal speciation since metals can occur in a variety of chemical forms such as metal free ions, metal complexes dissolved in solution, metal complexes adsorbed on other solids or metal precipitated into their own solids (Bodek *et al.* 1988). Partitioning of the heavy metal concentration into particulate and dissolved forms provides a basic indication of the likely toxicity, as it is the metals species in the dissolved fraction that are more readily bioavailable. However, factors such as acidity, the presence of organics and the solids concentration affect partitioning (Sansalone & Buchberger 1997b). Furthermore, mixing of runoff from different surfaces may alter the ratio of particulate and dissolved forms.

The largest proportion of the potential pollution load in urban runoff has traditionally been considered to come from the particulate fraction (Ashley *et al.* 2004). However, some investigations of the relationship between metals and TSS for road runoff have found limited correlations (Sansalone *et al.* 1995; Huang *et al.* 2007), or no correlations (Clark & Siu 2011). Table 2-2 summarises the proportion of metals in dissolved forms from different urban runoff types reported in international literature. It confirms that there is substantial variation in the metal partitioning between runoff types and locations and demonstrates the importance of understanding the partitioning characteristics of local runoff samples, which will influence appropriate stormwater management strategies.

Table 2-2: Literature-reported values for partitioning of heavy metals in urban runoff

Runoff Type	Reference Study	Study Location	Percentage in Dissolved Form			
			Cu	Pb	Zn	Other
Highway/Freeway	Sansalone *et al.* (1996)	Ohio, US	<50%	Approx. 50%	<50%	Al, Fe <50%; Cd, Ni > 50%; Cr approx. 50%
	Pitt and Maestre (2005)	Across US	31%	7%	26%	
	Kayhanian *et al.* (2007)	California, US	45%	16%	37%	
Urban road	Prestes *et al.* (2006)	Curitaba, Brazil	52%	18%		Cd 34%
	Helmreich *et al.* (2010)	Munich, Germany	21%		27%	Ni 17%
	Zuo *et al.* (2012)	Nanjing, China	40%		30%	
Road sediment	Stone and Marsalek (1996)	Sault Ste. Marie, Ontario, Canada	92%	71%	85%	Fe 15%; Mn 70%; Co 71%; Ni 9%; Cd 92%; Cr 12%
Rainwater	Garnaud *et al.* (1999)	Paris, France	57-100%	63-90%	84-100%	Cd 75-100%
Non-metallic roof runoff	Zobrist *et al.* (2000)	Switzerland	61%		48%	
	Quek and Förster (1993)	Bayreuth, Germany	49%	19%	73%	Cd 83%; Fe 2%
Mixed commercial	Pitt and Maestre (2005)	Across US	59%	31%	68%	

Dissolved metals in stormwater runoff can be more difficult to treat as the majority of the standard stormwater treatment systems are based on filtration or settling processes that primarily aim to remove sediment. A reduction in metal load is achieved in these systems by proxy as particulate metals are removed along with the sediment. However, dissolved metals may pass through these systems untreated.

Dissolved metals can be effectively treated in stormwater runoff provided a suitable treatment process is selected that facilitates processes of precipitation, sorption, filtration, or plant uptake and binding of the dissolved metals (LeFevre *et al.* 2014). Examples of systems that employ these processes include bioretention basins (LeFevre *et al.* 2014), carbonate/hydroxide dosing, wetlands (sulphide precipitation), proprietary organic/humic filters, gravel/rock biofilters and some engineered fabric filters. The performance of these systems varies with external factors such as temperature, runoff pH, and variations in redox conditions from fluctuations between wet and dry periods, and internal system factors such as media life expectancies, clogging and media cell structure (LeFevre *et al.* 2014). It is therefore important to characterise the partitioning of heavy metals in runoff to help guide management decisions and treatment selection.

2.2.5 Alkalinity

Alkalinity, while not considered a stormwater pollutant of concern, is an important stormwater quality parameter to characterise as it is a useful measure of the sensitivity of a waterway to receiving dissolved pollutants. Furthermore, the ecotoxicity of pollutants such as heavy metals and their trigger values (i.e. concentration limits used to indicate the threshold above which ecosystem values such as aquatic species diversity may not be adequately protected) for water quality change in response to the presence of alkalinity. Total alkalinity in urban runoff is typically sourced from calcium carbonate-containing materials, such as concrete. Kerb and channels, pavements and roofing tiles may all contribute alkalinity to urban runoff (Kaushal *et al.* 2013).

2.2.6 First flush phenomenon

The observance of a first flush phenomenon, where an elevated pollutant concentration occurs in the initial stages of a rain event, before concentrations lower to a steady state, has long been debated in stormwater literature. The first flush phenomenon is complex and site specific (Deletic 1998), and is influenced by a wide range of factors including rainfall characteristics (e.g. rainfall depth, intensity and length of antecedent dry period) and catchment characteristics (e.g. surface roughness, slope, time of concentration). Various studies have found positive evidence of a first flush effect on roof runoff (Förster 1999; Zobrist *et al.* 2000) and mixed runoff (Lee *et al.* 2002; Bach *et al.* 2010) while other studies have found no evidence of a significant first flush effect (Deletic 1998), however the assessment method of the first flush phenomenon also varies greatly across studies.

Stormwater discharge consent (i.e. permit) conditions often require the capture and treatment of a 'first flush' volume. For example, the Christchurch City Council's (CCC) Waterways, Wetland and Drainage Guide (Christchurch City Council 2012a) recommends as best practice the capture and treatment of the runoff generated by the first 25 mm of rainfall on a surface, with a minimum of 12.5 mm. This requirement has been derived from Auckland Council's assessment of the proportion of pollutants that would be removed by a representative treatment device over a range of storm sizes: treatment of the first 25 mm of each storm event was selected as a reasonable requirement as it would remove over 80% of the predicted pollutant load, while further increases in the treated storm depth would not achieve substantial gains in the level of pollutant removal (Auckland Regional Council 1992b). However, this treatment volume may not be wholly suitable for low intensity rainfall climates such as Christchurch's, as this requires the capture and treatment of *all* runoff from over 95% of Christchurch's rain events (Zollhoefer 2009). Indeed, a preliminary Christchurch study of the first flush phenomenon in urban runoff found that the runoff pollutant concentration had reduced to below relevant instream guideline values or were similar to near-surface groundwater concentrations within accumulated rainfall depths of 2-5 mm (Zollhoefer 2009).

The range of pollutant load is also valuable information for planning maintenance and defining the design capacity of the treatment system, as it is an indicator of how much pollutant mass will be detained in the system over time. This captured mass will ultimately influence performance and capacity of the treatment system.

2.3 Legislative framework and receiving water quality standards

2.3.1 Selected international approaches to stormwater quality legislation

Globally there has been a shift towards effects-based environmental legislation, where pollutant limits are set based on the sensitivity of a particular receiving environment to that pollutant. The means to achieve the limit are generally not prescribed, as legislators aim to enable more site-specific design, innovation and flexibility while ultimately achieving adequate environmental outcomes that each particular catchment requires for ecological health. Pollutant load models are valuable tools for the setting of appropriate pollutant limits as they provide predictions of the amount and distribution of pollution being contributed into the receiving environment from stormwater discharges. Accordingly, previous models have typically focused on this 'end-of-pipe' prediction of stormwater pollutant loads. However, if the effects of pollution are to be mitigated and receiving environment water quality limits achieved, at-source models are also needed that predict what pollution is generated where to guide source reduction and treatment before the runoff reaches its discharge point into the receiving environment. This section outlines various international approaches to legislating water quality management, as such legislation provides a key motivation for the characterisation and modelling of stormwater pollutant loads.

United States Environmental Protection Agency

The USEPA has developed a register of receiving water bodies that are considered to have impaired water quality, and now require all inflows to that water body to collectively meet the Total Maximum Daily Loads (TMDL) limits identified for pollutants of concern for that water body. The TMDL value is the daily incoming pollutant load that the water body is considered to be able to receive while still achieving relevant water quality standards. The TMDL limits are administered through the permitting of point and non-point sources.

The TMDL approach was introduced in legislation in the 1980s in response to growing recognition that while control of point source discharges had significantly reduced pollutant loadings, non-point source discharges remained largely unmanaged and were contributing a significant amount of pollution to receiving waters (Hoornbeek *et al.* 2008). The legislative framework requires states to develop a TMDL report for the catchment of each impaired water body that includes recommended actions for reducing the pollutant loadings in the catchment.

European Union Water Framework Directive

The European Union (EU) promulgated its Water Framework Directive in December 2000, which requires all EU member states to achieve ‘good’ qualitative and quantitative status of all water bodies (including marine waters up to one nautical mile from shore) (Commission of the European Communities 2000). ‘Good’ qualitative status is defined by several metrics quantifying the ecological and chemical status of surface waters, including:

- Biological quality (e.g. fish, benthic invertebrates, aquatic flora);
- Hydromorphological quality such as river bank structure, river continuity or substrate of the river bed;
- Physical-chemical quality such as temperature, dissolved oxygen and nutrient levels; and
- Chemical quality with catchment-specific pollutants and standards.

The catchment-specific standards to be developed by individual member states are to specify maximum instream concentrations for specific water pollutants. ‘Good’ status cannot be achieved if any one of the chemical pollutant standards is exceeded. It is essentially effects-based legislation that aims to holistically promote the sustainable use of all water, and therefore includes a focus on reducing environmental pollution to achieve long-term aquatic ecosystem health (Ashley *et al.* 2007). For example, Denmark uses a two-part approach to its environmental quality standards (EQS), with a long term EQS average concentration in the receiving waterway not to be exceeded over a year period and a short-term (24 h) EQS concentration that is allowed to exceed the long term EQS (Nielsen 2015).

Australia

Since the 1990s, the various states in Australia began developing guidelines for Water Sensitive Urban Design (WSUD; the integration of the urban water cycle elements, including stormwater, into urban planning and design to minimise environment degradation) (Roy *et al.* 2008). The national Australian government then developed a joint National Water Quality Management Strategy with New Zealand that led to the development of the Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines for protection of aquatic ecosystems (ANZECC 2000) as a benchmark for surface water quality and national guidelines for urban stormwater management (ANZECC & ARMCANZ 2000). However, stormwater management policies had largely already been developed by then by individual states (Roy *et al.* 2008) and stormwater management approaches remain largely on a state-by-state basis today. Within each state, the regulatory responsibility for watersheds may be shared across multiple levels of government; for example, in Victoria, authority for the management of a large watershed rests with the state water authority, however, the management of the smaller watersheds that drain into the large watershed rests with the local authority (Roy *et al.* 2008). The state environment agency mandates stormwater quality treatment on new development. For example, in Queensland, the State Planning Policy (SPP; Queensland Government (2014)) outlines construction-phase and post-construction phase stormwater management design objectives that include discharge quality limits for TSS, total phosphorus, total nitrogen and gross pollutants (only post-construction discharge limits for the latter three pollutants). The TSS limit is concentration-based for construction-phase discharges and a percentage reduction value in mean annual load from unmitigated development for post-construction discharges. There are no objectives or limits on heavy metals.

2.3.2 New Zealand legislation

National legislation

The chief body of environmental legislation in New Zealand is the Resource Management Act, enacted in 1991 (Ministry for the Environment 2010). It sets the requirement for effective environmental management of activities to ensure the effects of the activities on the environment are 'less than minor'. The objectives of the Act are achieved through a hierarchy of planning, policy and engineering documents at national, regional and city/district level. A schematic summary of the hierarchy is presented in Appendix B.

A National Policy Statement for Freshwater Management was issued by the central government in 2014, which directs local government to develop community-informed objectives for the state of waterbodies within their jurisdiction and to set limits to meet those objectives. National Environment Standards have been set for surface water quality that act as national bottom-line limits. However, Regional Councils are then required to develop plans for managing surface water resources (quantity and quality), that provide specific rules and water quality limits for each waterway within the region. These limits may be more stringent than the NES bottom-line limits.

Canterbury regional legislation

The Land and Water Regional Plan (LWRP; Canterbury Regional Council (2015)), sets the objectives, policies and rules regarding the water quality to be maintained in Canterbury natural waterways (including Christchurch urban waterways). It also sets the resource consenting requirements for stormwater discharges into these waterways (including when a consent is required, what parameters the consent may put limits on, and what matters can be taken into consideration when the consent application is processed by Council).

The LWRP Schedule 5 water quality standards are primarily based on the ANZECC guidelines for protection of aquatic ecosystems (ANZECC 2000). Table 2-3 summarises the relevant LWRP standards for the Avon and Heathcote catchments. Note that these values are for *instream* water quality outside of any mixing zone (i.e. these are values to be achieved once the discharge has had reasonable mixing with the receiving waterway) and do not apply to runoff prior to it entering the receiving waterway. However, they do provide a means of estimating the magnitude of stormwater issues in a catchment when these values are compared to untreated runoff quality.

Table 2-3: LWRP pollutant limits after mixing zone for spring-fed plains urban surface water

Pollutant	Guideline value
Dissolved Oxygen	≥70%
Dissolved Organic Carbon	Change <2.0 mg/L
Temperature	Avg. change ≤2.0 °C Maximum value of 20 °C
pH	6.5 - 8.5
Total suspended solids (TSS) [1]	50 g/m^3
Visual clarity [1]	Change <20%
Colour (Munsell units)	Change <5%
Dissolved Inorganic Nitrogen	<1.50 mg/L
Dissolved Reactive Phosphorus	<0.016 mg/L
E. coli	95% of samples <550 cfu/100mL
Dissolved copper [2]	1.8 µg/L
Dissolved lead [2]	5.6 µg/L
Dissolved zinc [2]	15 µg/L

[1] Where the background TSS concentration in the receiving waterway exceeds 50 g/m^3, the visual clarity requirement shall apply instead (Rule 5.95, LWRP).

[2] For 90% level of species protection, i.e. this is the threshold below which at least 90% of all aquatic species are not affected. This default value is to be modified for hardness based on measured alkalinity levels of waterway.

The LWRP also requires the Christchurch City Council (CCC) to develop integrated catchment management plans for the waterways within its jurisdiction. These ICMPs include a Stormwater Management Plan (SMP) that details how the policies and objectives of the various planning documents (e.g. the Greater Christchurch Urban Development Strategy and the Regional Policy Statement (framework for resource management in Canterbury region) will be implemented to achieve the stormwater-related planning and resource management goals for the area.

The SMP includes the proposed stormwater management strategies to mitigate adverse effects from stormwater on each subcatchment's receiving environment. An effective SMP can only be developed with good understanding of the pollutant generation processes, the composition of contributing impermeable surfaces and spatial distribution of pollution in each subcatchment.

Setting limits on stormwater runoff prior to discharge

In New Zealand, Auckland Council have recently moved to specifying Design Effluent Quality Requirements (DEQRs) in their proposed Auckland Unitary Plan (Auckland Council 2016). The DEQRs have been derived based on the performance that can reliably be expected from best practice BMPs (Auckland Council 2013) (Table 2-4). These are concentration-based limits for stormwater quality *prior* to discharge into the receiving environment. There are no provisions in these DEQRs for dissolved metal limits.

Table 2-4: Auckland Unitary Plan DEQRs for stormwater runoff management (modified from Auckland Council (2013)) for 90% of the annual rainfall

Receiving environment	Runoff quality by land use activity		
	Road, carpark	**Roofs**	**Industrial sites** [1]
River or stream	TSS < 20 mg/L	TCu < 10 µg/L	Site specific – appropriate to nature of activities, pollutants and receiving environment
	TCu < 10 µg/L	TZn < 30 µg/L	
	TZn < 30 µg/L	Temp < 25 °C	
	Temp < 25 °C		
All others	TSS < 20 mg/L	TCu < 10 µg/L	
	TCu < 10 µg/L	TZn < 30 µg/L	
	TZn < 30 µg/L		

[1] Industrial Sites refers to designated 'Industrial Sites Activity Area' under the Unitary Plan Maps

The Plan outlines whether stormwater runoff from any given surface is a 'Permitted', 'Controlled' or 'Restricted Discretionary' activity, depending on the activity type and size of surface generating stormwater runoff. 'Controlled' activities require the runoff to be managed by a stormwater treatment device that is designed to meet the DEQRs, while 'Restricted Discretionary' status is for all activities that fall outside of the 'Permitted' or 'Controlled' activity definitions. The assessment criteria for 'Controlled' and 'Restricted Discretionary' activities includes "whether stormwater pollutants are managed on-site or whether there are stormwater management devices in the catchment that can accept and cater for increased stormwater pollutant loads to meet mitigation requirements" (Auckland Council 2016).

Similar prescriptive approaches are being currently used in the Canterbury region as conditions of individual discharge permits for surface water discharges. It is possible that the CCC could take a similar approach in its SMPs as a means of controlling the pollutant loads in runoff that it accepts from individual landowners into its stormwater system, so it can achieve its obligations for the quality of its discharges from the Council-owned stormwater system into the receiving environment (i.e. under its catchment-wide stormwater discharge consents). This approach of requiring prescribed runoff quality prior to acceptance of the runoff into Council-owned stormwater infrastructure will require property owners to have a better understanding and prediction of pollutant loads and concentrations originating from their properties.

2.4 Stormwater quality management options

2.4.1 Overview of stormwater management approaches

The characterisation and modelling of stormwater pollutant loads is critical for the selection of appropriate management options, which typically seek to either reduce the pollutant concentration or reduce the volume of runoff, thereby reducing the pollutant load entering the receiving waterway. This section outlines the key principles of stormwater management that the characterisation and modelling research can contribute to, as well as outlining drivers provided by stormwater management requirements that have informed the structure of this research, including:

- Treatment systems only address specific pollutants – therefore the nature of pollutants must be understood to select an appropriate treatment approach;
- Each pollution ‘stream’ can be addressed in many ways (at source, or centralised for efficiency where appropriate) – understanding quality characteristics can help indicate what is most feasible and effective;
- Retrofitting is much needed in stormwater management but can be difficult due to constraints imposed by the existing land use. The existing surfaces (configuration, materials, conditions) need to be accounted for to enable stormwater quality improvements;
- There is a unique driver in Christchurch, New Zealand, with an opportunity to improve stormwater management on individual site scales as part of the post-earthquake rebuild in the city following the Canterbury Earthquake Sequence of 2010/11. Understanding the implications of typical past choices in stormwater management can guide better future choices; and
- The need to improve stormwater management in established urban areas (not just greenfield development) has guided the choice to develop an individual- (existing) surface-scale model.

Stormwater management can be considered to fall into three main categories: source reduction, on-site (small-scale) treatment and off-site (large-scale) treatment. Source reduction involves altering the characteristics of the surface (e.g. area, material, permeability) upon which runoff is being generated to reduce either the volume of runoff or the amount of pollution that is entrained in the runoff. Stormwater treatment techniques at any scale use a combination of physical, chemical and biological mechanisms to remove, reduce or, as in the case of organic compounds, break down pollutants. On-site treatment can encompass a wide range of treatment technologies and seeks to manage stormwater near to source, which provides benefits of smaller volumes, minimal conveyance, single-source runoff quality and enables private property owners to take responsibility and manage their runoff prior to it leaving their property. Off-site treatment (typically developed and maintained by local councils) also encompasses a wide range of treatment technologies but also enables large footprint systems such as wetlands to be employed. These large footprint systems have long hydraulic residence times and therefore are effective at removing a wide range of pollutants in both particulate and dissolved form (Martin 1988; Hatt *et al.* 2008) but require greater footprints and conveyance that on-site systems. Appendix C provides a summary of the wide range of structural and non-structural stormwater treatment options available, as well as how they function and which pollutants they most effectively immobilise.

Treatment techniques typically address only specific pollutants. Other non-targeted pollutants may pass through these systems unchanged (Aryal *et al.* 2010). Additionally, treatment performance is sensitive to several influent quality characteristics, including particle size, flow rate, volume and pH. Due to the varied nature of the pollutants (e.g. the physical nature of settleable solids in combination with metals in dissolved form), a treatment train of various components that target different pollutant types will likely be the most effective means of achieving an overall improvement in stormwater quality for large urban catchments.

2.4.2 Retrofitting

Retrofitting can be defined as the alteration of existing infrastructure to meet updated design criteria or levels of service (Watts 2011). It is particularly relevant to addressing stormwater issues in established urban areas, where historically little to no consideration for stormwater quality exists. Retrofitting within established urban areas must fit within constraints imposed by existing services (e.g. power, water infrastructure), property boundaries, land ownership and environmental conditions (e.g. soil infiltration rates). Guidance is therefore needed to identify priority areas for stormwater improvement and identify the nature of the stormwater pollutants, along with constraints imposed by existing urban development, such that appropriate policies and treatment systems can be selected.

The benefits from implementing stormwater management retrofits are becoming more widely recognised and can include water quality improvements, reduced flood risk, improved adaptability and resilience to future changes (e.g. land use, climate change), enhanced community environments and enhanced biodiversity (Digman *et al.* 2012). Typically the opportunity to retrofit for improved stormwater management comes with regeneration of urban areas, a process that occurs at varying scales and with limited facilitation by the local authorities. Christchurch is undergoing significant urban regeneration following the Canterbury Earthquake Sequence of 2010/11, which caused extensive damage to the city's built environment, including the stormwater network. Post-earthquake, there is opportunity with the city-wide restoration and rebuilding to incorporate more sustainable and resilient stormwater management. There are many examples of Water Sensitive Urban Design (WSUD) principles being incorporated into new developments in Christchurch. However, these new developments only form a fraction of the total urban area and therefore retrofitting within established urban areas will provide significant enhancement.

2.4.3 Overview of current stormwater management practice in Christchurch

Historically Christchurch's stormwater infrastructure has developed with the objective of providing flood protection and drainage of swampy land (NZine 2000; Christchurch City Council 2003; Watts 2011). The infrastructure includes underground piping, modified existing waterways (through concreting and timber-boxing), as well as artificial land drainage channels. These pipes and modified channels discharge untreated stormwater into the Avon River/Otākāro, Heathcote River/Opawāho, Avon-Heathcote Estuary/Ihutai or the sea. The ecological health of these receiving waterways is adversely affected by the pollutants carried in the stormwater, particularly sediment, heavy metals, nutrients and hydrocarbons.

Regular instream water quality monitoring has been undertaken by the CCC at 44 sites in the Avon and Heathcote catchments since January 2007. A recent review concluded that several sites have pollutant concentrations above instream guideline values, and included stormwater as a likely source of pollutants (Margetts & Marshall 2015). To further understand the contribution of stormwater to pollutants seen in Christchurch's urban waterways, CCC also began monitoring instream water quality at selected sites during one wet weather event each year since 2013. Margetts (2014) reports on wet weather sampling events undertaken to date (Table 2-5), in which sediment and heavy metal concentrations during these events were found to exceed concentrations observed in dry weather baseflow sampling.

Table 2-5: CCC wet weather water quality results for the Avon and Heathcote catchments

Parameter	***Instream:*** **Addington Brook, Avon catchment**		***Stormwater outfall discharge:*** **Waltham, Heathcote catchment**	**Relevant instream WQ guideline values**
	25 Mar 2014	**14 May 2014**	**14 May 2014**	
Total suspended solids (mg/L)	140	48	78	***50***
Total copper (µg/L)	34	8	850	***--***
Dissolved copper (µg/L)	18	3	103	***3.6***
Total lead (µg/L)	51	6	810	***--***
Dissolved lead (µg/L)	8	<1.5	5	***15.5***
Total zinc (µg/L)	210	130	1,867	***--***
Dissolved zinc (µg/L)	150	90	307	***29.7***

While best practice stormwater management systems, such as swales, stormwater detention ponds and wetlands are readily implemented in new greenfield developments (as a requirement of the LWRP (refer to Section 2.3.2)), it is more difficult to retrofit the established urban areas where the existing stormwater system has limited pollutant management. This difficulty comes from having more site constraints, including space limitations, existing land use activities, and integration with existing infrastructure and materials. These factors need to be considered in the planning and design of stormwater retrofits, as they influence their feasibility, cost and performance. A tool that assists with identifying pollutant ‘hotspots’ within an established urban catchment and assessing the expected benefits from implemented management options, will be of great assistance in developing effective, targeted stormwater improvement plans.

2.5 Stormwater quality modelling

2.5.1 Purpose of modelling

Stormwater quality modelling is a vital component in improved stormwater management as it enables characterisation of expected runoff quality, it informs receiving water quality analysis (e.g. identifies stormwater-sourced pollutants of concern to prioritise in instream monitoring), and guide decisions about source reduction policies and stormwater management infrastructure (Huber 1986). Historically, the vast majority of stormwater models have focused on stormwater quantity (i.e. they are hydrological models), and the ability to model stormwater quality is less developed and sophisticated. The complexity and variability of natural processes (including pollutant behaviour) can make the modelling process difficult (Elliott & Trowsdale 2007), however, estimation of pollutant loads is a key tool for practical uptake of improved stormwater management measures.

Stormwater quality models can be focused on understanding the long-term pollutant load entering the environment (e.g. on an annual timescale), or they can be focused on characterizing individual rain event-scale loads. Long-term pollutant loadings are indicative of the potential eco-toxicological effects of the pollutants on the receiving environment. Conversely, stormwater treatment selection and design is based on event loadings. Annual pollutant models may therefore be used to identify subcatchments where stormwater is contributing elevated levels of pollutants for the sensitivities of the receiving environment. Subsequently, event-based modelling of those targeted subcatchments can inform stormwater treatment design to reduce pollutant loads prior to entering the waterway and ultimately reduce the adverse impacts of runoff on the receiving environment.

2.5.2 Modelling techniques and key concepts

Pollutant build-up and wash-off processes

The accumulation, or build-up, of pollutants on an impermeable surface during dry periods is the result of interactions between several processes, including atmospheric deposition, wind erosion, surface material breakdown due to weathering and direct deposition of particles from vehicle wear (Zanders 2005; Egodawatta *et al.* 2009; Wicke *et al.* 2012b). During rain events, kinetic energy in the raindrops enables the entrainment and transportation of pollutants from the impermeable surfaces. Simultaneously, additional pollutants may enter the runoff from wet deposition, where the raindrops scavenge particles from the air as they fall (Sabin *et al.* 2005), or via dissolution of the surface material due to acidity of the rainfall (Quek & Förster 1993; Wicke *et al.* 2014). Rainfall characteristics, such as rainfall pH, rainfall intensity and the length of the dry period between rain events, therefore influence the amount of pollutants that build up and are washed off urban surfaces.

Most wash-off models assume that a pollutant has an initial mass on the impermeable area that existed before the rainfall (build-up) and a mass that remains after the rainfall. The wash-off mass is therefore the difference between the total mass and remaining mass.

Pollutant relationships with rainfall characteristics

Several studies have found correlations between the physical pollutant build-up and wash-off dynamics and climatic factors such as rainfall intensity, duration, depth and number of antecedent dry days (ADD). For example, total suspended solids (TSS) concentrations in road and highway runoff have been found to significantly correlate with average rainfall intensity (Barrett *et al.* 1998; Desta *et al.* 2007; Brodie & Egodawatta 2011)) as well as peak intensity (Crabtree *et al.* 2006; Brodie & Egodawatta 2011). Peak intensity has also been observed to correlate with TSS concentration from other runoff sources, including roofs (Gnecco *et al.* 2005; Brodie & Dunn 2010) and atmospheric deposition (Murphy *et al.* 2015). Total copper and zinc have been found to correlate with a variety of rainfall characteristics, suggesting this is sensitive to the local climate of the studied catchment.

Table 2-6: Summary of studies that have identified correlations between runoff pollutant levels and various rainfall characteristics

Runoff type	Reference	TSS [1, 2]	Total copper [1, 2]	Total zinc [1, 2]
Highway	Barrett *et al.* (1998)	INTavg, runoff volume	--	--
Urban runoff	Brezonik and Stadelmann (2002)	Dur, INTavg, Days since last event >25 mm	--	--
Urban runoff	Vaze and Chiew (2003)	INT	--	--
Roof, road	Gnecco *et al.* (2005)	INTpeak	--	--
Highway	Crabtree *et al.* (2006)	Depth, INTpeak	--	--
Highway	Desta *et al.* (2007)	INTavg	--	--
Carpark	Wicke *et al.* (2009)	ADD	ADD	ADD
Carpark, roof, road	Brodie and Dunn (2010)	Depth, INTpeak, less so: Dur, antecedent storm rainfall depth	--	--
Copper roof	He *et al.* (2001)	--	INT avg (power relationship)	--
Road	Brodie and Egodawatta (2011)	INTavg, INTpeak, Dur	--	--
Copper and zinc roofs	Wicke *et al.* (2014)	--	pH (power relationship)	pH (linear relationship)
Atmospheric deposition	Gunawardena *et al.* (2013)	Dry deposition: ADD; Bulk deposition: Depth	Traffic congestion	Traffic volume
Atmospheric deposition	Murphy *et al.* (2015)	INTpeak, Dur	Depth	Depth

[1] ADD: antecedent dry days; Depth: total event rainfall depth; Dur: event duration; INT: rainfall intensity (unspecified interval); INTavg: average rainfall intensity; INTpeak: peak rainfall intensity (5-min, 6-min or 10-min, varies by study)
[2] -- Indicates water quality parameter not included in study scope

Model types

Stormwater quality models are comprised of regression, stochastic or deterministic models. The majority of stormwater quality models use deterministic expressions to describe pollutant build-up and wash-off processes, using rainfall characteristics to predict the resultant pollutant contribution from impermeable surfaces (Deletic *et al.* 1997; Charbeneau & Barrett 1998; Egodawatta *et al.* 2007). Deterministic models produce a single value for any given set of input conditions (Obropta & Kardos 2007). Deterministic modelling typically employs mathematical replication equations, which assume that the rate at which the material is washed from a surface is proportional to the amount of material on the surface at the start of a rain event and that the rate can be described by a simple exponential equation (Sartor *et al.* 1974; Barrett *et al.* 1998; Egodawatta *et al.* 2007).

Statistically-based deterministic models can also be developed using linear regression modelling, where the output parameter (i.e. the dependent water quality parameter) is described by linear predictor functions incoporating multiple explanatory variables (i.e. independent rainfall parameters). Linear regression models enscapulate the complexity of processes contributing pollution, to find the optimum combination of independent variables that best fit the model. However, the relationships expressed are specific to the data used to derive them, and therefore the relationships may not be valid for other catchments so their application can be limited.

Stochastic models predict the output value based on the probabilistic distribution of the input variables, thereby inherently accounting for uncertainties in the input data. The fact that rainfall has a stochastic pattern and is a key driver of stormwater pollution generation has motivated the development of stochastic models for predicting stormwater pollutant loads (Rossi *et al.* 2005). Such models use the distribution of TSS mass during a rain event (as measured), an estimation of the available mass at the start of a rain event and the distribution of pollutant removal rates from treatment systems that the runoff passes through. The model outputs are valuable for predicting either the maximum pollutant concentrations that may occur during any given rain event (associated with acute environmental impacts) or the likely annual pollutant load entering the receiving environment (associated with long term chronic environmental impacts) (Rossi *et al.* 2005).

Model scale

Model structures can vary both spatially and temporally. In terms of temporal scale, models can predict pollutant loads or concentrations either as continuously simulated values, on a single rain event basis or as an annual load (Zoppou 2001; Auckland Regional Council 2010b). Continuous models simulate pollutant load over a long time period, and account for the continuous build-up and wash-off of pollutants across each time step using the principles of mass balance (James & Boregowda 1986; Zoppou 2001). An event model simulates results for an individual storm event. Annual load models use unit area pollutant load factors (based on published literature) to estimate the annual load for each pollutant. Continuous simulation and annual load models are typically used for planning purposes, such as development of integrated catchment management plans with specific stormwater treatment goals. Event models are typically used for assessing storm characteristics on specific pollutant loading, as well as informing the choice of best-fit stormwater treatment infrastructure.

Models also differ in terms of spatial scale; the majority of models aggregate the contributing area by land-use, with assumed unit area pollutant yields and scaling factors for density of impermeable surface cover. Alternatively, individual surface areas can be modelled, taking into account their individual surface characteristics such as surface material, age and condition and usage intensity (e.g. traffic intensity for roads, occupancy rates for carparks).

Other factors that influence the model form include:

- The objectives that the model is trying to help address, such as whether it is intended for use during stormwater management planning phase or for design and operation of stormwater treatment systems.
- The availability of input data and therefore the appropriate complexity of the model
- The intended end-user, as this influences the choice of model platform and the selected model outputs (e.g. maps, tables)

2.5.3 Overview of existing models

International models

Reviews of internationally available stormwater quality models by Zoppou (2001) and Elliott and Trowsdale (2007) summarise the different characteristics and scope of several stormwater models, as outlined in Table 2-7. Models vary in purpose from preliminary or detailed planning aids through to tools that focus on the effects of implementing different stormwater management options in a catchment.

The United States Environmental Protection Agency's (USEPA) Storm Water Management Model (SWMM) and eWater's Model for Urban Stormwater Improvement Conceptualisation (MUSIC) are two of the more common models used in the US and Australia, respectively. SWMM is widely used for the simulation of urban runoff quantity and quality. The model includes simulation of rainfall-runoff and routing through the stormwater network to discharge in a receiving waterway, while also simulating the build-up, wash-off, transport and treatment of key pollutants. It can be run as an event model or as a long-time continuous simulation (USEPA 2015). SWMM simulates pollutant load at a subcatchment scale, with the user defining the proportion of different land use covers within the subcatchment and the input parameter values for the build-up and wash-off functions to be used for each land use type.

Likewise, MUSIC is widely used in Australia for pollutant load estimation and assessment of the effect of implementing stormwater management scenarios. The model represents the inflow of pollutants from various source areas as nodes, using a stochastic approach with dry weather and wet weather event mean concentrations (Dotto *et al.* 2011). MUSIC then uses a rainfall-runoff model to route the pollutant through user-selected treatment scenarios. The source areas are defined in the model by land use and area (i.e. it is an aggregated subcatchment-scale model). MUSIC assigns default values for the associated properties of these land use types, such as total impervious fraction, average slope, time of concentration, maximum rainfall intensity and annual rainfall, or the user can provide catchment-specific calibrated values for any of these attributes. The model can be run at time steps down to 6 minute intervals and up to 24 hours duration.

Table 2-7: Summary of selected internationally available urban models (adapted from Elliott and Trowsdale (2007) and Zoppou (2001))

Model name	Primary intended use
InfoWorks	Detailed model for planning and preliminary design
MIKE URBAN	Detailed model for planning and preliminary design
MOUSE	Detailed simulation of urban drainage
MUSIC (Model for Urban Stormwater Improvement Conceptualisation)	Conceptual design for drainage systems, with emphasis on treatment devices
P8-UCM	Estimation of stormwater pollutant load
PURRS (Probabilistic Urban Rainwater and Wastewater Reuse Simulator)	Single site water use model
RUNQUAL (Runoff Quality for Development Sites)	Preliminary planning or education
SLAMM (Source Loading and Management Model)	Planning tool for load of pollutants
StormTac	Management of lake catchments and conceptual design of stormwater treatment
SWMM (Storm Water Management Model)	Detailed model for planning and preliminary design
UVQ (Urban Volume and Quality)	Integrated water cycle, water reuse
WBM (Water Balance Model)	Planning-level assessment of water quantity

While these internationally available models are sophisticated and many are comprehensive in their scope, their complexity and need for detailed input data (e.g. catchment hydraulics), or their aggregation of surfaces to a subcatchment level, poses a restriction to their use. A balance is needed between accuracy and reliability of the model outputs against the time and cost of obtaining the required input data.

New Zealand models

At a national scale, the Auckland Regional Council (ARC) has developed the Pollutant-Load Model (CLM) (Auckland Regional Council 2010a) to estimate annual pollutant loads in post-treatment stormwater runoff, although it is acknowledged the model was developed for the Auckland regional climate only. The National Institute of Water and Atmospheric Research (NIWA) has expanded upon the CLM model with the Catchment Pollutant Annual Loads Model (C-CALM), a GIS-based model for calculating annual pollutant load post-treatment (Semadeni-Davies *et al.* 2009). However, Christchurch-specific stormwater models are limited; Elliot developed a model for preliminary catchment scale planning of urban stormwater quality controls focused on the Christchurch environment (Elliot 1998), while Fifield (2011) assessed options for retrofitting low impact urban design structures in existing urban areas within the Avon River catchment. Table 2-8 summarises the key features of the New Zealand models.

Table 2-8: Summary of local models and their key features

Model name	Primary objective	Modelled water quality parameters										Temporal scale	Spatial scale
		TSS	**BOD**	**TN**	**TP**	**Total Cu**	**Total Zn**	**Total Pb**	**Hydrocarbons**	**Dissolved Cu**	**Dissolved Zn**		
Fifield's model	Identify best options for stormwater retrofit low impact designs that best fit Christchurch's land use and climatic conditions.	✓	✓	✓	✓	✓	✓	✓	✓			Annual load	Urban – applied to individual streets, individual carpark areas and a mixed-use subcatchment
Elliot's model	Identify the lowest cost stormwater quality improvement option across each subcatchment, subject to constraints that include meeting sediment guidelines, flood prevention and maximum pond sizing limits.					✓	✓					Annual load	Urban – subcatchments calculated then combined to give overall catchment load
ARC's CLM	Estimation of stormwater pollutant loads for large urban areas.					✓	✓		✓			Annual load	Urban and rural fringes – catchments >20 ha
NIWA's C-CALM	Identify the rates and effects of long-term pollutant delivery and accumulation in receiving environments.	✓				✓	✓			✓	✓	Annual load	Urban or rural – subcatchments, can be combined to give overall catchment load

2.5.4 Limitations of existing models

Existing New Zealand models such as CLM and C-CALM are annual load calculating models and therefore do not identify the expected amount of pollutants in stormwater runoff from an individual storm event. While annualised load models are useful in quantifying the cumulative effects of pollutants in discharges, event-based models are useful in identifying the peak loads that treatment systems need to be designed to handle (i.e. capacity design) as well as indicating storm conditions under which acute effects on the environment could be expected from large event loads. Under legislative frameworks such as the US's Total Maximum Daily Load requirements (see Section 2.3.1) or Auckland Council's Design Effluent Quality Requirements (see Section 2.3.2), an event-based load model is needed, rather than an annual model, to inform development of an appropriate management approach.

Furthermore, existing models all simulate on a subcatchment or catchment scale. While this is valuable for catchment-scale planning, this does not support individual property owners who may wish to implement source reduction measures or on-site treatment to meet environmental permitting requirements placed on them by local government or to reduce their pollution footprint. Subcatchment scale models are also limited in their ability to spatially identify the distribution of pollutant loads across a catchment, including 'hotspot' areas that would benefit most from targeted stormwater management improvements.

It is also well recognised that a stormwater quality model needs to allow for local climatic conditions, as parameters such as rainfall intensity and rainfall pH influence the pollutant generation (Liu *et al.* 2013). If annual load models are to be applied in different climatic areas, then the unit area pollutant yield rates need to be adjusted for local conditions.

Heavy metal partitioning between dissolved and particulate form is an important indicator of the potential environmental effects of stormwater runoff as well as directing the types of treatment processes that would be effective at reducing the pollutant loads (refer to Section 2.2.4). Currently, most local models do not model dissolved metals. Dissolved metal loads are a more indicative measure of aquatic ecotoxicity than total metal loads (as dissolved metals represent the bioavailable form of the metal), and therefore there is value is representing dissolved metals within a stormwater quality model. Additionally, the treatment technologies that are effective at removing dissolved metals differ significantly from those that can remove particulate metals, and therefore modelling of the dissolved portion will assist appropriate treatment selection.

2.6 Chapter summary

The literature reviews shows that untreated runoff characterisation and event-based modelling of the associated pollutant loads are valuable components of developing an effective, targeted stormwater management approach for reducing the impact of stormwater pollutants on urban waterways. However, there are gaps in current knowledge that need to be addressed, specifically:

1. The influence of a low rainfall intensity climate on pollutant generation from different impermeable urban surfaces, as rainfall conditions and surface characteristics are known to influence pollutant build-up and wash-off processes;
2. The variation of particle size distribution, both during an individual rain event and between multiple events, as this variation presents a treatment performance risk in sediment removal treatment systems;
3. Development of a modelling framework that can predict event-based pollutant loads from individual surfaces, based on rainfall characteristics. Event load predictions are needed to guide the development of targeted management approaches, including source reduction policies and the selection and design of treatment systems;
4. Inclusion in the model framework of metal partitioning predictions, as this informs the selection of appropriate treatment processes; and
5. Inclusion in the model framework of a spatial component for assessing the location of hotspot areas within a catchment to be targeted for stormwater improvements.

3 Methodology

3.1 Overview

This chapter outlines the methods of sample collection, lab analysis and measured rainfall characteristics used to develop a dataset of untreated runoff quality for the Okeover catchment in western Christchurch, New Zealand. The dataset has then been used to characterise TSS and heavy metals (see Chapters 4 and 5) and to inform the development and calibration of a pollutant load modelling framework (see Chapter 6). Specific details on statistical methods such as regression analysis are provided at the start of the relevant results chapters. Also note that the sampling methodology for the Addington Brook catchment model application (Chapter 7) is provided within that chapter, as it necessarily differs from the methodology used to develop the Okeover dataset.

Untreated runoff samples were collected from four different impermeable surfaces within the catchment (a concrete tile roof, copper roof, galvanised roof and asphalt road) and analysed for TSS, particle size distribution and heavy metals. The concrete roof and road runoff samples were also analysed for total alkalinity. General screening analysis for total acidity, total ammonia, dissolved reactive phosphorus (DRP) and chemical oxygen demand (COD) was also completed at the start of the sampling programme but discontinued as results were generally not elevated (refer to Appendix D for further details).

The untreated runoff quality monitoring methodology aimed to:

1. Develop a database of local (Christchurch, New Zealand) untreated runoff quality from various impervious surface types, for a range of typical rainfall events expected annually;
2. Record the rainfall characteristics under which each sample was collected; and
3. Assess the observed distribution of pollutant concentrations from each surface type

3.2 Case study catchment description: Okeover catchment, Christchurch

The Okeover Stream catchment covers 61 ha of established urban area in Christchurch city, New Zealand. The Okeover Stream is a first-order tributary of the Avon River. The upper catchment receives stormwater contributions from an established residential area, while the University of Canterbury campus covers most of the lower part of the catchment (Figure 3-1). The main impervious surfaces contributing stormwater runoff are roofs, roads (with a range of traffic intensities), and carparks (with some on-street parking and some large university campus carparks) (Table 3-1). Other surfaces that may potentially contribute runoff are hardstand areas such as driveways on private property or overland flow from grassed and garden areas, however, these are not considered in this research as their contributions to surface runoff are uncertain (e.g. runoff is able to partially infiltrate the surface, or surface flow runs into adjacent permeable grassed or garden areas) but expected to be small.

Figure 3-1: Location map of Okeover catchment, Christchurch, New Zealand

Table 3-1: Summary of Okeover catchment contributing impermeable surfaces

Surface material type		Total Area[1] (m²)	Percentage of contributing area for surface type	Percentage of overall contributing area
Roof surfaces		***146,400***	***100%***	***59.3%***
Butynol roof		3,652	2.5%	1.5%
Concrete roof		35,439	24.2%	14.3%
Copper roof	(old)	856	0.6%	0.3%
Decramastic	(new)	3,863	2.6%	1.6%
	(moderate)	9,038	6.2%	3.7%
	(old)	4,262	2.9%	1.7%
Galvanised roof	(new)	46,390	31.7%	18.8%
	(moderate)	17,712	12.1%	7.2%
	(old)	8,960	6.1%	3.6%
Glass roof		5,234	3.6%	2.1%
Zincalume® roof	(new)	989	0.7%	0.4%
	(moderate)	8,281	5.7%	3.4%
	(old)	1,724	1.2%	0.7%
Road surfaces		***62,300***	***100%***	***25.2%***
Coarse asphalt		62,300	100%	25.2%
Carpark surfaces		***38,330***	***100%***	***15.5%***
Coarse asphalt		38,330	100%	15.5%

[1] Areas estimated from Okeover MEDUSA model which delineates individual roof, road and carpark areas in GIS (refer to Chapter 6)

3.3 Sampling locations and collection equipment set-up

3.3.1 Locations

Stormwater sampling locations (Figure 3-2) were selected to provide runoff data from different surface materials: a concrete tile roof (a common residential roofing material), a copper roof (used as an architectural material), a galvanised roof (a common industrial, commercial and residential roofing material) and a coarse asphalt road (most common road surface in the city; the road has an annual average daily traffic count of 11,000 (Christchurch City Council 2012b)) (Figure 3-3 and Table 3-2). The four sites were in close proximity to each other such that they can be considered to have been exposed to the same climate characteristics, including antecedent dry period and rainfall conditions for each sampled event. Other secondary factors also considered were:

1. Suitability of access to collection point;
2. Safety of people deploying and maintaining sampling equipment at the site; and
3. Likelihood that equipment would not be interfered with by others

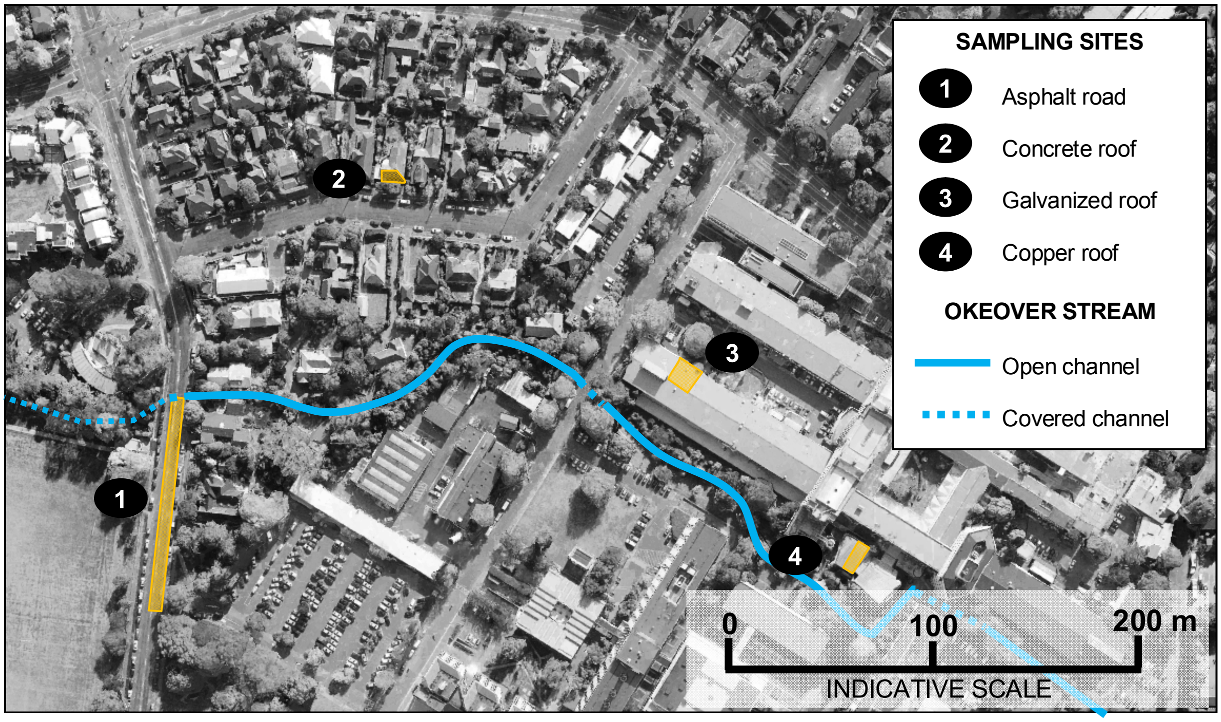


Figure 3-2: Location of sampling sites, Okeover catchment, Christchurch, New Zealand

Figure 3-3: The four sampled surfaces: 1) asphalt road, 2) concrete roof, 3) galvanised roof, 4) copper roof

Table 3-2: Summary of surface characteristics for sampling locations

Surface	Location	Estimated contributing surface area (m^2)	Indicative age	Roughness	Orientation
Concrete tile roof	Residential	45	Approx. 60 years	Coarse	South
Copper roof	University campus	90	Approx. 40 years	Smooth	South/East
Galvanised roof	University campus	130	Approx. 15 years	Smooth	North
Asphalt road	Residential feeder road	800	Approx. 10 years	Coarse	--

3.3.2 Collection equipment

A combination of grab sampling and automatic sampling (ISCO 6712C Compact Portable Automatic Sampler) was used to capture untreated runoff during the peak initial conditions (first flush, FF; defined as the first 2 L of runoff, following Wicke *et al.* (2014)), transitional and steady state (SS) conditions (Figure 3-4).Pollutant concentrations were generally observed to reach a 'steady state' concentration after typically 45 minutes (refer to Chapter 4, Section 4.3.4 for further detail), with continuing direct deposition from vehicles and the low intensity rainfall resulting in a relatively consistent concentration during the recession period of the storm event. Up to 2 L of runoff was collected for each sample, as dictated by the volume requirements of the analyses conducted for each sample.

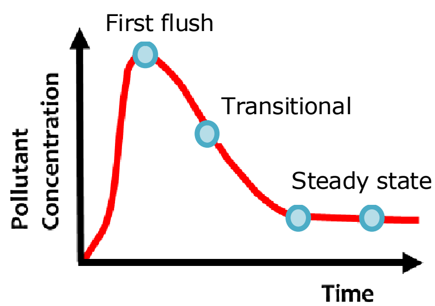


Figure 3-4: Condition descriptions used for time-series sampling

Figure 3-5 shows the set-up used for collection sites where an autosampler was used to collect runoff (the three roof sites). This method enabled up to 6 time-series samples to be collected during a single storm event. The autosampler was triggered to begin sampling via a liquid level actuator sitting in the collection basin. The time of each autosampler sample was recorded electronically by the autosampler.

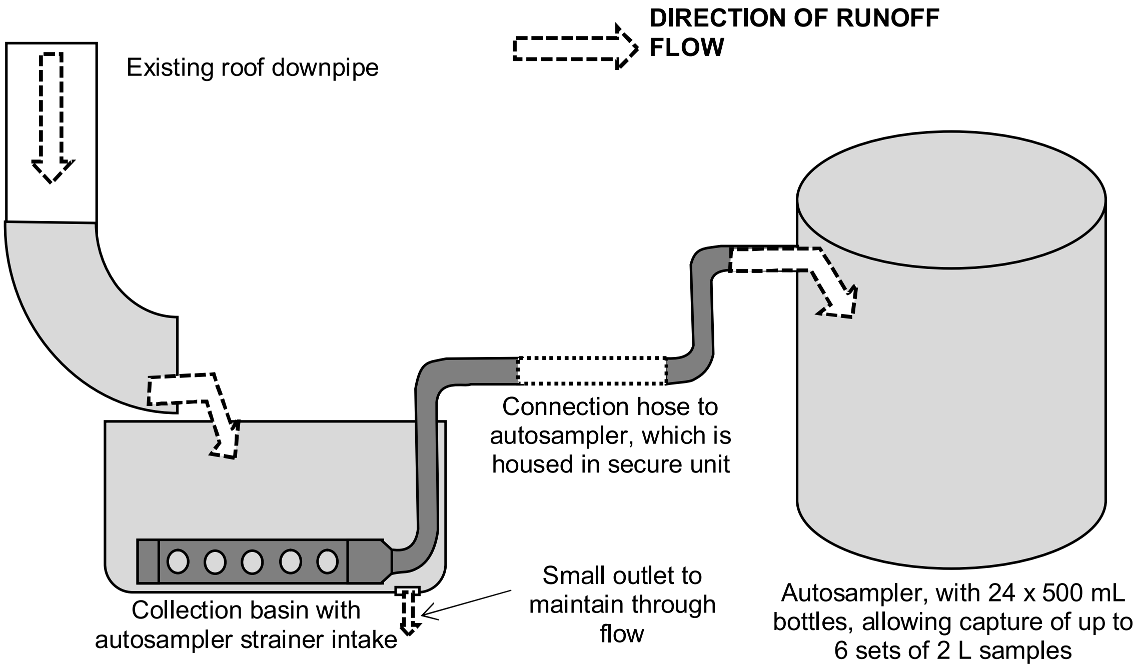


Figure 3-5: Schematic of sample collection set-up from roof sites using autosamplers

For sites where grab sampling was employed (all road samples and some roof samples), samples were taken of the FF runoff at the start of an event, then at recorded time intervals thereafter. It was observed during initial sampling that there was a significant time lag between the start of rain and arrival of the initial runoff at the sampling point (the sump) for both the road and concrete roof surface due to initial absorbance of rain by the asphalt/concrete surface until saturation was reached. By comparison, runoff was almost immediate from the smooth galvanised and copper roof surfaces.

Potential sampling biases towards finer sediments (as coarse sediment settle out more readily) were minimised by this sampling methodology which enabled the full stream of runoff to be collected directly from a downpipe (for the roof sampling sites) or as it overflowed into a roadside sump (for the one road sampling site). The use of time-weighted sampling was considered appropriate as the time of concentration was generally low due to the limited surface area that contributed to each downpipe or sump. The rainfall depth over the time interval when each sample was taken could then be used to derive a pollutant load without requiring flow data (see Chapter 6, Section 6.3.2 for further detail). The time interval between samples was selected to characterise the change from FF to SS (typically taken at 0, 15, 30, 60, 120, 180 minutes).

3.3.3 Sample treatment

For grab sampling, 1 L HCl-acid-washed containers were used to collect samples via an acid-washed intermediary 200 mL container. These were taken directly back to the lab and stored in a refrigerator (at 4°C).

Each autosampler used 24 x 500 mL HCl-acid-washed containers. Autosampler-collected samples were taken back to the lab as soon as possible after the autosampler programme was complete and stored in a refrigerator (at 4°C). This timing varied depending on when the programme finished (i.e. relative to daylight hours, as health and safety requirements meant field work was not undertaken at night).

3.4 Stormwater runoff quality analytical methods

3.4.1 Overview of parameters tested

Table 3-3 summarises the analytical methods used for each parameter, in accordance with the Standard Methods for Examination of Water and Wastewater jointly produced by the American Public Health Association (APHA), the American Water Works Association (AWWA) and the Water Environment Federation (WEF).

Table 3-3: Record of stormwater runoff quality analytical methods

Parameter	Units	APHA method	Brief description	Detection range
TSS	mg/L	2540 D	Vacuum filtration with 1.2 µm filter paper, then oven-dried at 105°C for 1 hour.	> 3
Total metals digestion (metals preparation)	N/A	3030 E	Boiling nitric acid. For preparation of metals for ICP-MS analysis.	--
Filtration (metals preparation)	N/A	3030 B	Sample filtration through 0.45 µm and preserved with nitric acid. For preparation of metals for ICP-MS analysis. Dissolved metals were filtered prior to preservation; total metals were filtered post-digestion.	--
Total Copper	µg/L	3125 B	Method 3030 E, 3030 B, ICP-MS (trace level)	> 1
Total Zinc	µg/L	3125 B	Method 3030 E, 3030 B, ICP-MS (trace level)	> 10
Total Lead	µg/L	3125 B	Method 3030 E, 3030 B, ICP-MS (trace level)	> 1
Dissolved Copper	µg/L	3125 B	Method 3030 B, ICP-MS (trace level)	> 1
Dissolved Zinc	µg/L	3125 B	Method 3030 B, ICP-MS (trace level)	> 10
Dissolved Lead	µg/L	3125 B	Method 3030 B, ICP-MS (trace level)	> 1
Total Alkalinity	mg/L as $CaCO_3$	2320 B	Titrate 200 mL sample with 0.01 N HCl to pH 4.5	> 1
Particle size analysis	µm on volume basis	-	Laser diffraction measurement of particles	0.1 – 3,000

Table 3-3 to Table 3-5 outline the number of samples analysed from each sampling site for the different water quality parameters. Not all surfaces were sampled for all events due to troubleshooting with sampling equipment during initial stages of sampling. Also, during the later sampling events, sampling was targeted to specific surface types where additional data was needed to more accurately describe the contaminant concentrations during specific conditions (e.g. more first flush data during high intensity rain was required for copper roofs).

Table 3-4: Summary of samples analysed for TSS and heavy metals

Event	Date	Analyte	Surfaces sampled (no. of time-series samples)			
			Concrete roof	**Copper roof**	**Galvanised roof**	**Asphalt road**
1	8 Dec 2013	TSS	***4***	-	-	-
2	17 Dec 2014	TSS, metals	2	-	***4***	-
3	20 Jan 2014	TSS, metals	***6***	-	***5/6***	2
4	26 Jan 2014	TSS, metals	***6***	-	***3***	-
5	5 Feb 2014	Metals (Cu, Gv)	-	***1***	***1***	-
6	12 Feb 2014	TSS, metals	1	1	1	1
7	14 Feb 2014	TSS (Cr), metals (Cr, Cu)	1	-	1	-
8	4 Mar 2014	TSS, metals	6	7	7	3
9	16 Mar 2014	TSS, metals	***7***	***7***	***6***	***3***
10	25 Mar 2014	TSS, metals	-	***2/3***	***1***	-
11 [a *]	25 Mar 2014	TSS, metals	***6***	***7***	***5***	***4***
12	5 Apr 2014	TSS, metals	***5***	-	***5***	-
13	5 May 2014	Metals (Cu)	-	***1***	***4***	-
14	8 May 2014	-	-	-	-	-
15	26 May 2014	TSS, metals	-	***2/3***	***3***	***4***
16	6 Jun 2014	TSS, metals	-	***1***	-	-
17	9 Jun 2014	TSS, metals	***8***	6	-	3
18	16 Jun 2014	TSS, metals	***2***	***2***	-	***2***
19 *	25 Jun 2014	TSS, metals	***4***	***3***	***2***	***5***
20 *	3 Oct 2014	TSS	2	2	2	2
21	18 Oct 2014	TSS	-	***1***	***2***	***1***
22 *	22 Nov 2014	TSS	1	***2***	***2***	***2***
23 *	10 Dec 2014	TSS	1	1	1	1
24 *	9 Feb 2015	TSS		***1***	***1***	***1***
25 *	6 Mar 2015	TSS	***3***	-	***3***	***4***
		No. of events where FF captured	13	12	15	10
		No. of event where SS captured	17	12	17	13
		Total no. of events captured	17	17	20	15

Bold italics indicates event where first flush samples were collected

5/6, for example, indicates 5 samples analysed for TSS, 6 analysed for metals

[a] Second rainfall event started 4 hours 20 mins after previous event. Review of the pollutant concentrations suggested that this should be considered an independent rain event with short ADD period, as new FF and SS conditions were observed.

* Indicates all four surfaces sampled for that particular rain event

Table 3-5: Summary of samples analysed for Particle Size Distribution (PSD)

Event	Date	Surfaces sampled (no. of time-series samples)			
		Concrete roof	**Copper roof**	**Galvanised roof**	**Asphalt road**
8	4 Mar 2014	-	-	-	3
9	16 Mar 2014	1	***1***	-	-
13	5 May 2014	-	***1***	***4***	-
14	8 May 2014	***4***	-	***4***	-
15	26 May 2014	-	***3***	***3***	***4***
16	6 Jun 2014	-	***1***	-	-
17	9 Jun 2014	***7***	6	-	3
18	16 Jun 2014	***2***	***2***	-	***2***
19 *	25 Jun 2014	***4***	***3***	***2***	***5***
20 *	3 Oct 2014	2	2	2	2
21	18 Oct 2014	-	***2***	***2***	***1***
22 *	22 Nov 2014	***2***	***2***	***2***	***2***
23 *	10 Dec 2014	1	1	1	1
24 *	9 Feb 2015	***1***	***1***	***1***	***1***
25 *	6 Mar 2015	***3***	***3***	***3***	***4***
No. of events where FF captured		**7**	**10**	**8**	**7**
No. of events where SS captured		**8**	**7**	**9**	**8**
Total no. of events captured		**10**	**13**	**10**	**11**

* Indicates all four surfaces sampled for that particular rain event

Table 3-6: Summary of samples analysed for total alkalinity

Event	Date	Surfaces sampled (no. of time-series samples)		
		Concrete roof	**Galvanised roof**	**Asphalt road**
1	8 Dec 2013	***4***	-	-
2	17 Dec 2014	-	***4***	-
3	20 Jan 2014	***6***	***6***	2
4	26 Jan 2014	***6***	-	-
6	12 Feb 2014	1	-	1
7	14 Feb 2014	1	-	-
8	4 Mar 2014	6	-	3
9	16 Mar 2014	***7***	-	***3***
11	25 Mar 2014	***6***	-	***4***
12	5 Apr 2014	***5***	-	-
15	26 May 2014	-	-	***4***
17	9 Jun 2014	***7***	-	***3***
18	16 Jun 2014	***1***	-	***2***
19	25 Jun 2014	***4***	-	***4***
No. of events where FF captured		**9**	**2**	**6**
No. of event where SS captured		**11**	**2**	**9**
Total no. of events captured		**12**	**2**	**9**

3.4.2 Total suspended solids

Samples were vacuum-filtered through pre-weighed 1.2 μm glass fibre filter papers. Where possible, coarse leaf material was excluded (following the method of Stone and Marsalek (1996)). The filter papers were placed in an oven (at 105 °C) and dried for 1 hour, and then the combined TSS and filter paper were weighed. The resultant difference in weight (i.e. the TSS) was converted to concentration (mg/L) by accounting for the volume of sample used, as follows:

$$TSS = \frac{Mass_{(solids+filter)} - Mass_{(filter)} + Mass_{(loss)}}{Volume\ of\ sample} \quad (3\text{-}1)$$

At least two method blanks were done in each batch, using deionised water, to identify the weight of glass fibre washed out of the filter paper during each filtration. An average of the blanks' results was then added onto each sample's weight to account for this loss of glass fibres. All TSS analyses were completed within 48 hours of sample collection.

3.4.3 Total and dissolved metals

Unfiltered 60 mL subsamples were taken for total metals analysis and preserved with trace grade nitrate acid to lower the pH to ≤2. 25 mL subsamples were also taken for dissolved metals analysis and filtered through a 0.45 μm syringe filter, then preserved with trace grade nitrate acid to pH ≤2.

Following acid preservation and refrigeration, total metal samples were prepared for analysis by acid digestion: 5 mL of trace grade nitric acid was added to 25 mL of preserved sample and the mixture was digested on a heating block at 105°C for 1 hour. The digested mixture was then allowed to cool and a 10 mL subsample was filtered through a 0.45 µm syringe filter into a vial. For dissolved metals, a 10 mL subsample of each preserved dissolved metal sample (including method blank) was placed into a vial.

Samples were then analysed for total and dissolved metals using an inductively coupled plasma-mass spectrometer (ICP-MS; Agilent) at the University of Canterbury within two months of preservation, in accordance with Method 3125-B (APHA 2005). Certified reference material (NIST, seawater), replicates and blanks were included in each analysis batch.

Due to the addition of 5 mL nitric acid during the digestion process, which diluted the sample by 12.5 % i.e. 5 mL into 25 mL), the ICP-MS result for each total metal was multiplied by 1.2 to account for the dilution.

3.4.4 Total alkalinity

Alkalinity is generally not expected to be high in the runoff, but it is important to quantify the potential contribution from concrete-based materials (i.e. cement as the calcium carbonate source) as ecotoxicity and trigger values for water quality change in response to the presence of alkalinity.

Samples were titrated with 0.01 N HCl until pH 4.5 was reached, and the amount of HCl titrant was recorded (in accordance with SM2340 (APHA 2005); pH readings taken with EDT RE357Tx Microprocessor). Total alkalinity (mg/L as $CaCO_3$, respectively) was calculated using as follows:

$$Total\ alkalinity = \frac{Vol_{titrant} * N * 50{,}000}{Volume\ of\ sample} \qquad (3\text{-}2)$$

where N is the strength of the titrant. All total alkalinity analyses were completed within 14 days of sample collection.

3.4.5 Particle size distribution (PSD) analysis

A Horiba LA-950 laser diffraction analyser was used to measure the PSD on a volume basis (range of 0.1 – 3000 µm). Laser diffraction measures the angular variation in the intensity of light being scattered as a laser beam passes through the sample. Small particles scatter the light at large angles, while large particles scatter the light at small angles. The measured angular variation in light intensity is then used to calculate the particle sizes using Mie light scattering theory (Horiba 2004). Mie theory uses the optical properties of both the particles and the medium they are dispersed in to derive the distribution of the particles. Samples were analysed for PSD within 6 hours of collection, following a study by Li et al (2005) which found that substantial particle aggregation could occur in samples held longer than 6 hours.

Selection of particle size distribution analysis method

Several methods have been used historically to measure PSD and there is little consistency in approach. Each method has its own advantages that suit characterisation of either fine, coarse or well-graded sediments, vacuum-sediment samples or suspended sediment in runoff samples (Table 3-7). The laser diffraction analyser method used here provided benefits of being able to analyse a wide range of particle size (0.1 – 3,000 μm), good repeatability could be achieved for each sample and it allowed a common method to be applied across samples from different surfaces such that PSD could be compared across different urban impermeable surfaces. It could also be done within the constraints of the available 2 L sample size (with other analyses also needing to be done from the 2 L).

Table 3-7: Common particle size analysis techniques

Technique	Advantages	Limitations
Sieve analysis	Can be used for wet or dry particles, directly applicable results to filtration-based treatment system design	Dry sieving: drying sediments prior to sieving can alter particle size and character (Krein & Schorer 2000). All sieving: fraction size bins are large compared to diffraction or electrical resistance methods.
Sedimentation	Directly applicable results to sedimentation-based treatment system design (Li *et al.* 2005)	Labour intensive
Laser diffraction (dynamic light scattering)	Can measure a wide range of particle sizes, including down to 1 nm	Sensitive to user-selected refractive index
Particle counter (electrical resistance)	Results are not affected by particle's shape, nature, gravity and refractive index (Li *et al.* 2005)	Carrier fluid may promote coagulation; method may disrupt fragile flocs (Li *et al.* 2005)

Selection of refractive index

Suspended particle composition has a significant influence on how light scatters, and inorganic and organic particles have very different refraction indices. It is known that heterogeneity of particles within a sample affects the light scattering and particle size distribution results. A study by Andrews *et al.* (2010), on the role of particle composition on accurate particle size analysis found waters composed of a wide variety of particle sizes, shapes and compositions could be reasonably analysed for particle size distribution using an inorganic refraction index of 1.56 (i.e. 1.17 * RI_{water}) + 0.0001i.

It is the finest particles that show the greatest dependence on the refraction index value, and the largest effects, due to polarisation of the light (Andrews *et al.* 2010). This is because they scatter light at wider angles, and so are more influenced by particle non-sphericity (Liu *et al.* 2003). The laser diffraction machine assumes that the non-spherical particles in the sample are randomly oriented such that it is measuring a range of the possible cross-sections of these particles (Andrews *et al.* 2010).

3.5 Quality assurance/quality control

Quality assurance/quality control (QA/QC) measures have been included as part of the sampling in this research to ensure the sampling is meaningful and the results are reliable. Duplicates were generated for TSS, total metals, dissolved metals, PSD and ammonia, at a ratio of at least one duplicate for every ten samples for each sampled event. Method blanks (i.e. blanks where deionised water was used as the sample equivalent and the same lab procedure was carried out on the blank as for the other actual samples) were done for TSS, total metals, dissolved metals, ammonia and COD.

The Relative Percent Difference (RPD) was calculated from each duplicated sample, using Eqn. 3-4.

$$RPD = \frac{Difference}{Average} = \frac{X_2 - X_1}{(X_1 + X_2)/2} \tag{3-4}$$

All samples were found to have an RPD value less than ±25%. The highest proportion of elevated RPD values were seen in copper and galvanised roof runoff TSS samples, where significant relative variation in mass could be expected when the TSS concentration of the sample is low.

For the heavy metal duplicates, there were no RPD values greater than ±10% for total or dissolved metals for any galvanised roof or road duplicates. The copper roof only had RPD values greater than ±10% for total lead, while the concrete roof samples did have RPD values greater than ±10% (only one >25% RPD, for the SF17 total zinc sample). Again, the concrete roof had low concentrations of heavy metals and therefore it is more likely to get a larger relative percent difference when the values are low. Appendix E provides a summary of the duplicate results and RPD values.

3.6 Health and safety

A Health and Safety Plan was developed prior to starting sample collection, to address specific risks and identify mitigation actions to be taken when working near waterways, roads, during rain events, and working alone. The plan was reviewed and approved by the Department of Civil and Natural Resource Engineering's Safety Manager, and implemented each time field work was done. Key components included the use of a sign-out/sign-in buddy system, daylight sampling only, use of a hi-visibility vest around traffic and warm, weatherproof clothing.

A Lab Induction with the Environmental Lab Manager was also completed prior to starting any lab analysis. The lab is classified as a Hazardous Substances Exempt Lab, meaning it complies with

Hazardous Substances (Exempt Laboratory) Regulations 2001 requirements, including the appropriate storage, handling and management of hazardous substances.

3.7 Sampling event characteristics

In this research, the build-up and wash-off of pollutants was studied under naturally occurring rainfall conditions. Each sampling event was characterised by its rainfall pH, average intensity, peak 5-min intensity, length of antecedent dry period (ADD), rain event duration, depth of sampling event, and depth of previous rain event (Table 3-8). A Campbell® weather station was installed for this purpose and is located within the Okeover catchment on a balcony on the south end of the University of Canterbury's (UC's) Department of Civil and Natural Resources Engineering building, approximately 25 m from the copper roof sampling site. The weather station reads in 5 minute intervals. The weather station was used to measure and record all rainfall characteristics except for rainfall pH, which was conducted manually. The average intensity was calculated as the average of the hourly intensities recorded over the whole rain event.

Table 3-8: Summary of rainfall characteristics for sampling event

Event no.	Date of sampling	Rainfall pH (S.U.)	Average intensity (mm/hr)	Peak 5-min intensity (mm/hr)	ADD (days)	Rainfall duration (hr)	Total depth (mm)	Depth of previous event (mm)
1	8 Dec 2013	5.90	2.82	9.96	10.82	3.6	10.1	1.6
2	17 Dec 2013	7.86	1.27	4.92	4.10	3.4	4.4	0.2
3	20 Jan 2014	7.78	0.68	3.84	13.53	14.3	9.7	0.3
4	26 Jan 2014	5.78	0.46	2.28	3.07	6.4	2.9	0.4
5	5 Feb 2014	6.46	0.80	1.32	9.30	0.3	0.2	4.2
6	12 Feb 2014	6.35	3.41	19.56	3.60	4.0	13.6	1.0
7	14 Feb 2014	6.33	0.20	1.32	1.10	5.1	1.0	14.9
8	4 Mar 2014	6.35	4.61	16.80	0.60	31.3	144.2	0.4
9	16 Mar 2014	6.38	3.00	14.40	10.46	16.3	41.2	144.2
10	25 Mar 2014	5.58	0.20	0.20	6.11	0.1	0.2	0.4
11	25 Mar 2014	5.58	3.20	9.60	0.18	2.9	9.2	0.2
12	5 Apr 2014	5.98	1.47	4.80	10.74	3.6	2.2	1.6
13	5 May 2014	6.01	1.60	2.40	5.60	0.3	0.4	1.8
14	8 May 2014	5.93	0.65	2.40	3.32	5.7	3.6	0.4
15	26 May 2014	5.86	2.40	7.20	0.63	4.9	5.2	1.4
16	6 Jun 2014	6.26	0.30	2.40	0.32	1.3	0.4	0.6
17	9 Jun 2014	5.82	1.37	7.20	0.22	31.4	43.0	1.2
18	16 Jun 2014	5.46	2.40	2.40	3.90	0.3	0.8	16.4
19	25 Jun 2014	5.81	1.48	4.80	7.27	1.1	1.6	5.8
20	3 Oct 2014	5.74	2.03	4.80	5.41	1.1	2.2	0.4
21	18 Oct 2014	5.10	0.56	2.40	5.41	3.6	2	1.2
22	22 Nov 2014	5.67	0.526	1.56	2.81	2.4	1.3	4.4
23	10 Dec 2014	5.93	0.80	2.40	0.21	1.3	1.0	1.2
24	9 Feb 2015	6.31	0.90	2.40	3.56	0.7	0.6	4.4
25	6 Mar 2015	6.05	1.41	4.80	3.17	4.3	6.0	0.8
Mean value		**6.09**	**1.54**	**5.45**	**4.61**	**6.0**	**12.3**	**8.4**
Median value		**5.93**	**1.37**	**3.84**	**3.56**	**3.6**	**2.2**	**1.2**
Minimum value		**5.10**	**0.20**	**0.20**	**0.18**	**0.1**	**0.2**	**0.2**
Maximum value		**7.86**	**4.61**	**19.56**	**13.53**	**31.4**	**144.2**	**144.2**

The UC weather station data was compared against meteorological records from the National Institute of Water and Atmosphere's (NIWA) Weather Station, 2.2 km from the sampling sites, and found to be similar and therefore representative of rainfall conditions for wider Christchurch. The NIWA station data was used when the UC weather station data was not available for maintenance reasons.

Rainfall pH

Wet deposition pH is a common indicator for rainwater acidity (Bridgman, 1989), with complex interactions and processes contributing to the overall rainfall acidity. Raindrops scavenge carbon dioxide from the atmosphere as they fall, dissolving into carbonic acid, which has a pH at equilibrium of 5.6. Sulphur and nitrogen oxides (sourced from fossil fuel combustion) further contribute sulphuric and nitric acid resulting in lower pH values. Rainfall pH was measured along with the other water quality parameters since it can influence the contribution of metal dissolution to stormwater metal loads.

Rainfall pH was measured for each event from rainfall captured by a wet deposition sampler (N-Con ADS Model 00-120-2; lidded sampler bucket with electronic moisture sensor that triggers lid to be retracted from the bucket during rain) adjacent to the copper roof site, using a pH meter (EDT RE357Tx Microprocessor). The pH reading was taken as soon as practicable during or after the rain event. The rainfall pH of the sampled events centres around pH 5.9 and overall has a relatively narrow range extending from pH 5.1 to pH 7.9 (Figure 3-6). This pH range is globally typical for 'normal' rainfall (i.e. non-acid rain), and is similar to ranges previously observed both within the Okeover catchment and elsewhere in New Zealand (Table 3-9).

Table 3-9: Selected urban rainfall pH records

Rainfall pH range / *mean*	Location	Reference
International		
4.25 – 5.08	Sydney, Australia	Ayers and Gillett (1984)
5.64	Izmir, Turkey	Al-Momani *et al.* (1995)
3.5 – 6.8	Hong Kong	Sequeira and Peart (1995)
5.3 – 6.2	Switzerland	Zobrist *et al.* (2000)
6.25	Delhi, India	Balachandran and Khillare (2001)
4.1 – 5.6	Sweden	Karlen *et al.* (2002)
6.6 – 8.0	Germany	Athanasiadis *et al.* (2007)
New Zealand		
4.6 – 6.7	Taita, Lower Hutt	Miller (1961)
4.1 – 6.5	Rotorua	Fish (1976)
4.5 – 6.5	Kelburn, Wellington	Holden and Clarkson (1986)
4.7 – 6.5	New Plymouth	Ayers *et al.* (1986)
5.8 – 7.0	Auckland	Pennington and Webster-Brown (2008)
4.9 – 7.2	Okeover catchment, Christchurch	Wicke *et al.* (2012b) (*n* = 42)
5.1 – 7.9	Okeover catchment, Christchurch	This study (*n* = 25)

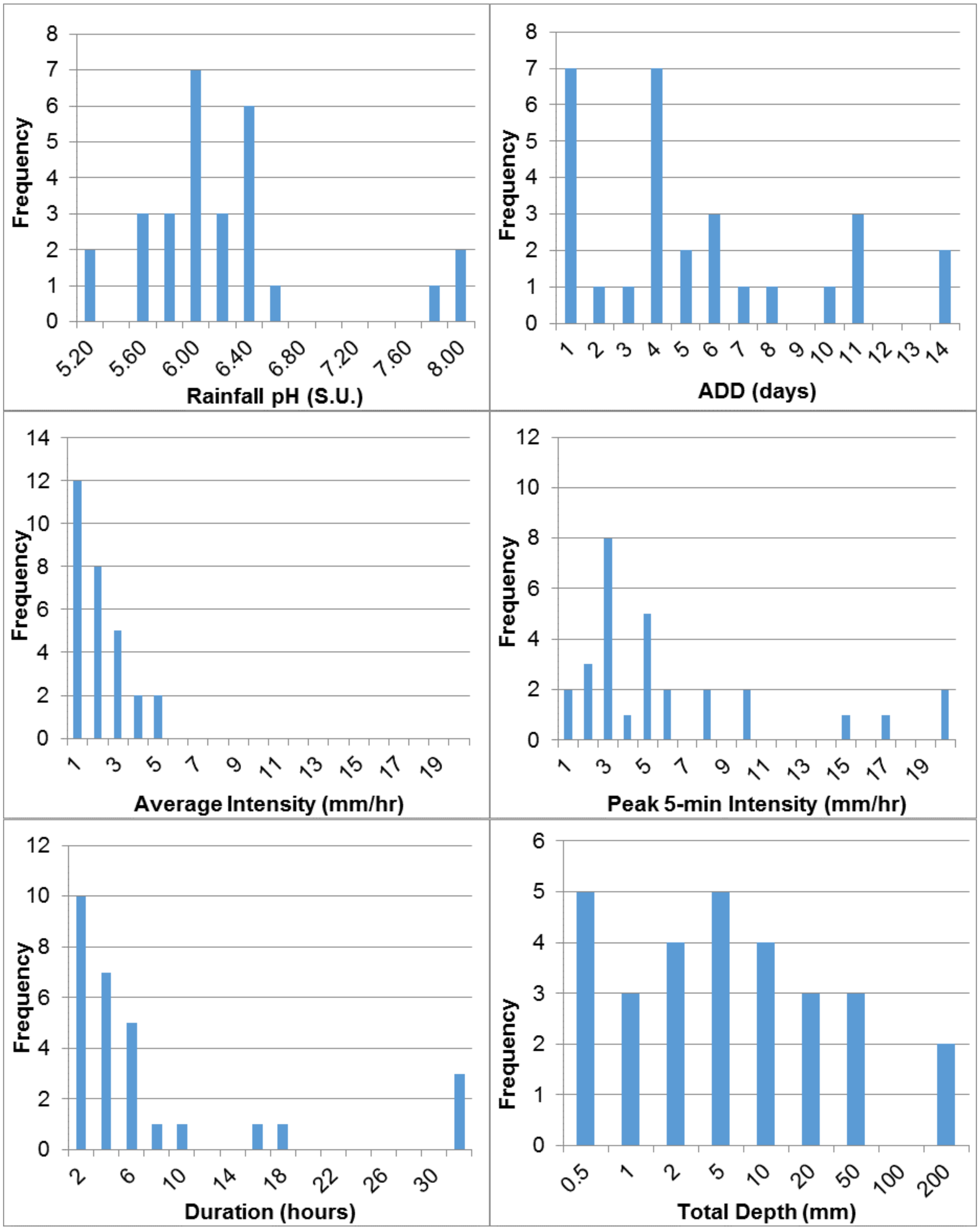


Figure 3-6: Distribution of rainfall event characteristics for all sampled events

Rainfall intensity

Rainfall intensity is an indication of the kinetic energy present that allows the entrainment and transport of particles in runoff from a surface (Egodawatta *et al.* 2007). The average intensity of the sampled events centre around 1.4 mm/hr (Figure 3-6), which is considered a 'light' rainfall intensity on a global scale. It ranges from 0.2 mm/hr ('light rain' or 'drizzle') to 4.6 mm/hr ('moderate rain'). This range of sampled event intensities is within typical intensities expected for Christchurch: based on historic rainfall data, 95% of rain events ≥6 hr duration in Christchurch have an intensity ≤5.1 mm/hr (NIWA 2011). In comparison elsewhere in New Zealand, Auckland's rainfall intensity is >8 mm/hr for equivalent events, and both Hamilton and Wellington are >6 mm/hr; however, Dunedin is also <5 mm/hr (NIWA 2011). Average intensities reported in international studies are higher than the intensities observed in this study (with the exception of the rainfall characteristics recorded in a study within an arid climate zone) (Table 3-10).

Antecedent dry days

The number of antecedent dry days (ADD) has been observed to be correlated to the amount of pollutant build up on a surface for a variety of climates (Kayhanian *et al.* 2003; Wicke *et al.* 2009; Gunawardena *et al.* 2013). ADD of the sampled events has two peaks at 1 and 4 days (Figure 3-6), with an overall range from <1-14 days. While this range of ADD compared similarly with reported ADDs from a study conducted in a temperate climate zone in the US, other climate zones generally showed longer ADDs (Table 3-10).

Depth and duration

The range of event depth and duration is strongly skewed to low total depth-short duration rain events (Figure 3-6). International studies have typically reported comparatively higher rainfall depth to duration characteristics (due to high average event intensities) (Table 3-10). For example, a study in Queensland, Australia (Herngren *et al.* 2005) reported duration ranging from 0.08-8.4 hours but the lowest recorded average event intensity was 5.3 mm/hr (with other events exceeding 25 mm/hr average intensity).

Comparison of rain events to long term climate records

Events sampled during this research encapsulated all seasons within a 15-month time period. The sample events' rainfall intensity, depth and duration were reviewed against the Annual Exceedance Probability (AEP) values developed for the catchment by NIWA's High Intensity Rainfall Design System Version 3 (HIRDS.V3) (NIWA 2011). Only one sampled event, Event 8 (4 March 2014), could be considered an extreme event under this definition (Figure 3-7). This event had a rainfall depth and average rainfall intensity which met or exceeded the predicted 10% AEP and 5% AEP rain events, respectively, for the catchment.

Table 3-10: Reported rainfall characteristics in runoff quality studies (range and median)

Climate zone	Reference	Study location	Average intensity (mm/hr)	Maximum intensity (mm/hr)	ADD (days)	Depth (mm)	Duration (hours)
Humid continental	Sansalone and Buchberger (1997b)	Cincinnati, OH, US			4-20 (10)	0.4-25 (7.8)	0.2-6.6 (3.3)
Humid subtropical	Barrett *et al.* (1998)	Austin, TX, US				140	11.8
	Herngren *et al.* (2005)	Queensland, Australia	5.3-52.7 (10.7)		0.1-26.5 (1.6)		0.08-8.42 (1.42)
Mediterranean	Han *et al.* (2006)	West Los Angeles, CA, US	0.2-11.3 (2.2)	3-61 (15.2)	0.3-192 (35)	1.5-156 (19.4)	2-47.5 (8.6)
Arid	Taebi and Droste (2004)	Isfahan, Iran	0.7-1.3 (1.0)	1.5-4 (2.7)		2-7.3 (5.0)	2.6-6.6 (4.9)
Temperate	Bannerman *et al.* (1996)	Madison, WI, US	6-233 (72)		0.3-9.8 (5.3)	15-213 (79)	0.12-12.84 (1.5)
	This study	Christchurch, New Zealand	0.2-4.6 (1.4)	0.2-19.6 (3.8)	0.2-13.5 (3.6)	0.2-144 (2.2)	0.1-31.4 (3.6)

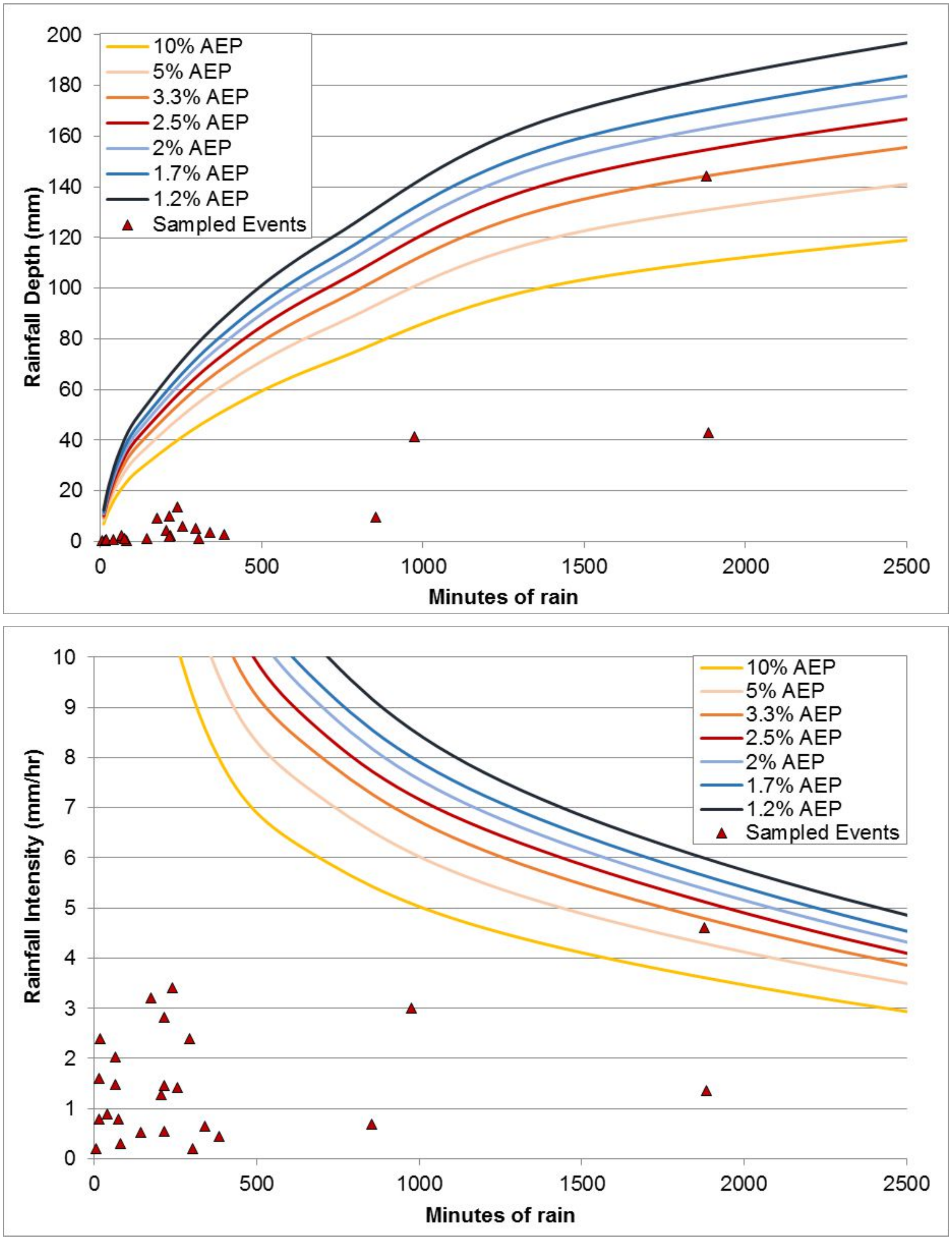


Figure 3-7: Rainfall frequency spectrum for Okeover catchment against sampled event characteristics

4 Sediment and Heavy Metal Characteristics of Untreated Urban Runoff

4.1 Introduction

Untreated runoff quality is known to vary with surface material type (and other surface factors such as condition, age and orientation of the surface), as well as climatic factors such as rainfall pH, intensity, number of antecedent dry days and duration (refer to Chapter 2: Section 2.5.2). Only a limited number of studies have considered runoff quality from a range of different surfaces in the same geographical area, with most studies considering runoff aggregated by land use or runoff from exclusively roof or road surfaces. Therefore, there is a need to assess such relationships using data collected from both roof and road surfaces exposed to the same climate conditions within the same catchment. This data is important in developing the MEDUSA model for predicting loads from individual surfaces in a catchment for the purposes of optimising stormwater treatment.

Most stormwater quality studies reported in literature have typically been for moderate to high intensity rainfall events (> 5 mm/hr, whether natural or simulated rainfall). Christchurch's climate is semi-arid with a mean annual rainfall of 647 mm/yr and an annual average of 85 wet days (defined as rain ≥1 mm) (NIWA 2013a). 95% of rain events in the catchment with duration ≥ 6 hours are ≤ 5.1 mm/hr intensity (NIWA 2011) and so are classified as low intensity.

Various studies have identified correlations between pollutant wash-off rates and climatic variables such as rainfall intensity (road runoff: Crabtree *et al.* (2006); Barrett *et al.* (1998); Kayhanian *et al.* (2003), roof runoff: Yaziz *et al.* (1989)). The contribution of low intensity rainfall to pollutant wash-off is not well understood as low rainfall intensities may affect pollutant contributions from each surface differently due to their varying physical and chemical properties.

This chapter presents untreated runoff quality results and detailed analysis from the field work undertaken in the Okeover Stream catchment (refer to Chapter 3). The key aims of this section of the research were:

1. Describe and compare pollutant concentrations from different impermeable urban surfaces that are within a close spatial proximity so that they are exposed to the same atmospheric deposition and (low) rainfall intensity rainfall conditions;
2. Collect data from real-world surfaces under natural rain conditions to capture the overall natural variation that occurs;
3. Identify any statistically significant differences in runoff quality between the surfaces, as well as between initial and steady state samples for the same surface;
4. Identify the transition time to steady state conditions for each surface;
5. Provide a detailed comparison of the data with published pollutant concentrations from international literature;
6. Identify correlations between total and dissolved partitioning of heavy metals for each surface type; and

7. Identify correlations between TSS and total heavy metals for each surface type.

4.2 Methodology

4.2.1 Overview

A full description of the sampling sites and the techniques used for sample collection, lab analysis and statistical analysis is provided in Chapter 3. An overview of the pertinent aspects of the methods used to generate and analyse the TSS and heavy metal datasets discussed in this chapter is provided here:

Untreated runoff samples were collected from 24 rainfall events (all events <4.7 mm/hr average intensity) from four impermeable surfaces within a mixed residential/institutional catchment in western Christchurch, New Zealand. The sampling was conducted over a 15 month period from December 2013 to March 2015. The samples were analysed for TSS, total and dissolved Cu, Pb and Zn and total alkalinity (see Chapter 3: Section 3.4 for detailed analytical procedures). Analyses were also done for As, Cd, Cr and Ni, however, as concentrations were found to typically be below relevant instream guideline values, not further analysis was done. Some limited screening tests were done for total ammonia, acidity dissolved reactive phosphorus (DRP) and chemical oxygen demand (COD). However, these tests were discontinued as results showed these parameters were not present at elevated levels in the runoff. Appendix D provides a summary of the additional parameter results (As, Cd, Cr, Ni, total ammonia, dissolved reactive phosphorus, acidity and COD). The remainder of this chapter refers only to TSS, Cu, Pb, Zn and alkalinity results.

Due to sampling logistics, a full set of analytes could not always be tested in each sample (e.g. insufficient sample volume could be collected). However, there were 12 sampling events where all four surfaces were sampled concurrently. Priority was typically given to TSS analysis over total and dissolved metals and alkalinity. Nevertheless, substantial datasets were developed for TSS and heavy metals for the four surface types (Table 4-1 and Table 4-2), and for alkalinity in concrete roof and asphalt road runoff (Table 4-3).

Table 4-1: Number of samples collected for TSS analysis

Sample Type	Surface type				*Total*
	Concrete roof	Copper roof	Galvanised roof	Asphalt road	
First flush	10	11	14	9	***44***
Transitional	19	8	14	6	***47***
Steady state	36	26	30	23	***115***
Total	***65***	***45***	***58***	***38***	***206***

Table 4-2: Number of samples collected for heavy metals analysis

Sample type	Surface type				*Total*
	Concrete roof	Copper roof	Galvanised roof	Asphalt road	
First flush	8	10	11	5	***34***
Transitional	17	9	12	5	***43***
Steady state	29	24	26	17	***96***
Total	***54***	***43***	***49***	***27***	**173**

Table 4-3: Number of samples collected for alkalinity analysis

Sample type	Surface type				*Total*
	Concrete roof	Copper roof	Galvanised roof	Asphalt road	
First flush	9	--	2	5	***16***
Transitional	17	--	1	5	***23***
Steady state	30	--	7	17	***54***
Total	***56***	***--***	***10***	***27***	**93**

4.2.2 Statistical analysis methods

Statistical analysis was done using IBM®'s SPSS® Statistics (Release 22.0) software. A summary of the datasets used in this Chapter's data analysis is provided in Appendix F.

Comparison of differences across the four surfaces

Kruskal-Wallis tests were performed to identify whether statistically significant differences collectively exist in the TSS, total Cu, total Zn or total Pb concentrations between different surface types. This non-parametric test was selected as this method allows for unequal sample sizes across the different surfaces and residuals were unlikely to be normally distributed. Visual inspections of box-plot distributions of TSS and heavy metal concentrations for each surface were used to confirm that the distributions were not similar between surfaces, and therefore only mean ranks (and not medians) could be compared between the different surfaces. The Kruskal-Wallis method ranks each datapoint for the dependent variable (i.e. the water quality parameter) irrespective of which surface it is associated with (Kruskal & Wallis 1952). For each surface, it then finds the mean of all that surface's rank values. Pairwise comparisons of the difference in mean rank were then performed using Dunn's (1964) procedure with a Bonferroni correction for multiple comparisons to further identify which particular surfaces differed significantly from each other.

Comparison of first flush to steady state concentrations

Initial and steady state samples for each event were compared for each surface type to identify whether there was a significant difference indicating a first flush effect. As flow data was limited, a statistical analysis of paired initial and steady state data for each event was used instead of a mass-volume relational analysis (Maestre *et al.* 2004). Paired t-tests were conducted to assess whether the pairs were statistically correlated. Analysis of the boxplots of the pairwise differences showed that there were no outliers. The data was log-transformed to meet the requirement for the pairwise difference to achieve a normal distribution, confirmed with Shapiro-Wilk analysis.

Relationship of total to dissolved metal concentrations

Total and dissolved metal concentrations were compared for each sample (grouped by surface type) to assess if there was any correlation between the metal fractions (i.e. particulate or dissolved) on the basis of surface type, using Pearson's product-moment correlation. Scatterplots were used to confirm the presence of a linear relationship between the data, the data was log-transformed to meet the assumption of normality (confirmed with Shapiro-Wilk analysis) and the data was screened for outliers prior to correlation analysis. Only one datapoint (a copper roof first flush sample from Event 9) was found to be an extreme outlier for all three metals and it was consequently removed from the dataset as it was considered to compromise the rest of the copper roof dataset (remaining n = 43).

Relationship of TSS to total heavy metal concentrations

The relationships (if any) between TSS and the various total metal concentrations were explored using Pearson's Product-Moment Correlation analysis. Data was checked for outliers using scatterplots of TSS versus each total metal. One first flush copper roof sample from Event 9 and one first flush asphalt road sample from Event 18 showed as outliers on all scatterplots due to their unusually high heavy metal concentrations. These two samples were removed from the dataset. The data was log-transformed for normality and confirmed with Shapiro-Wilk analysis and Q-Q plots.

4.3 Results

4.3.1 Sampled event characteristics

Rainfall pH had a median value (and range) of 5.96 (5.1 – 7.9). Event average rainfall intensity, antecedent dry period (ADD), duration and total event depth all showed left-skewed distributions, with median values and ranges as follows: event average rainfall intensity 1.4 (0.2 – 4.6) mm/hr, ADD 3.8 (0.2 – 13.5) days, duration 3.5 (0.1 – 31.4) hours and total depth of 2.2 (0.2 – 144) mm. The dataset included the March 2015 event which exceeded the 5% AEP intensity for the catchment (see Chapter 3: Section 3.7).

4.3.2 Comparison between surfaces

Total Suspended Solids

There were obvious differences in TSS concentrations between different surfaces types for both first flush and steady state samples (Table 4-4). TSS concentrations for each surface were confirmed to be significantly different from each other ($X^2(3)$ = 62.795, p <0.001) when using the Kruskal Wallis analysis. Subsequently, post-hoc analysis identified statistically significant differences between all surface pairs except for concrete and copper roofs, and concrete and galvanised roofs (Table 4-5).

Road runoff was found to generally have an order of magnitude or higher steady state TSS concentrations than any of the roof surfaces (Figure 4-1). The road first flush TSS concentration was similar to that from the copper roof first flush; however, because the copper roof *steady state* runoff was an order of magnitude lower than that of the road runoff, this shows that the overall event load per area from a road surface was higher than from a copper roof surface.

Table 4-4: Median and ranges of TSS and total metals concentration for different surface types, and mean ranks from post hoc tests

Surface Type	TSS			Total Cu			Total Zn			Total Pb		
	n	Median (Range) (mg/L)	Mean rank*	*n*	Median (Range) (µg/L)	Mean rank	*n*	Median (Range) (µg/L)	Mean rank	*n*	Median (Range) (µg/L)	Mean rank
Concrete roof	*65*	2.8 (0.1 – 30.8)	79.4	*54*	8.3 (2.2 – 27.8)	67.2	*54*	15.3 (5.4 – 44.5)	41.7	*54*	3.2 (1.1 – 12.6)	106.6
Copper roof	*45*	8.0 (0.2 – 453)	112.3	*43*	1,298 (423 – 7,861)	152	*43*	27.9 (5.0 – 292)	64.2	*43*	2.2 (0.3 – 108)	83.6
Galv. roof	*58*	3.0 (0.1 – 22.3)	76.1	*49*	5.2 (2.5 – 13.5)	41.2	*49*	376 (75 – 2,369)	145.9	*49*	0.8 (0.2 – 5.7)	43.8
Asphalt road	*38*	63.2 (6.6 – 327)	176.1	*27*	26.3 (7.0 – 84.3)	106.3	*27*	102 (20.2 – 429)	107.1	*27*	7.2 (0.4 – 45.4)	131.5

* See Section 4.2.2 for description of mean rank (dimensionless)

Table 4-5: Post hoc test significances on Kruskal-Wallis analysis for comparisons of differences between surfaces

Pairwise combination of surface types	Adjusted significance			
	TSS	Total copper	Total zinc	Total lead
Concrete roof – copper roof	0.053	<0.001 *	1.000	1.000
Concrete roof – galvanised roof	1.000	0.004 *	<0.001 *	<0.001 *
Concrete roof – asphalt road	<0.001 *	0.067	0.004 *	<0.001 *
Copper roof – galvanised roof	0.005 *	<0.001 *	<0.001 *	<0.001 *
Copper roof – asphalt road	<0.001 *	0.003 *	0.023 *	<0.001 *
Galvanised roof – asphalt road	<0.001 *	<0.001 *	0.001 *	<0.001 *

***** Denotes statistically significant result. The significance level is 0.05.

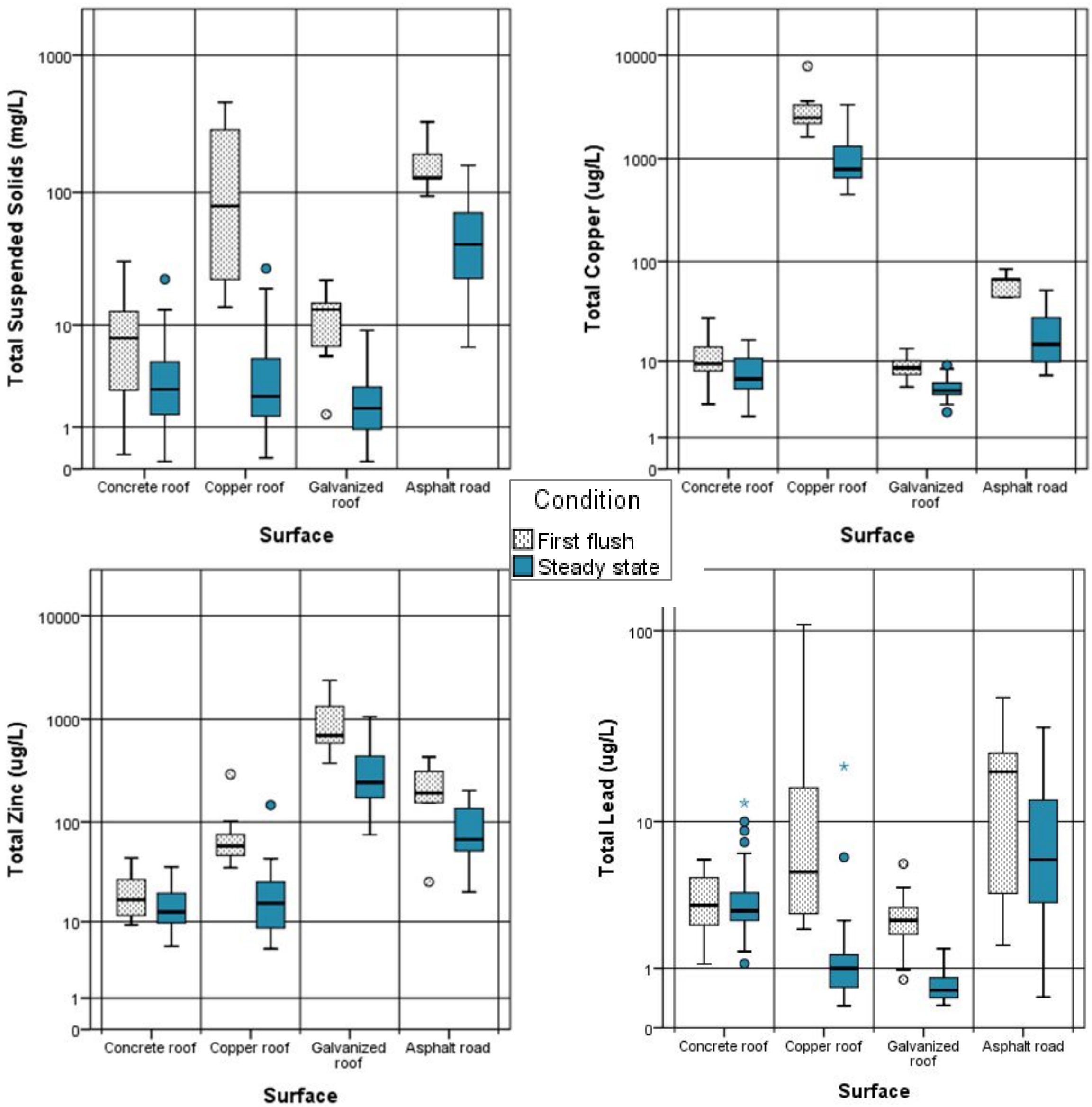


Figure 4-1: Distribution of TSS and selected (Zn, Cu, Pb) heavy metal concentrations for each surface type (° denotes outliers ± 1.5x Inter Quartile Range (IQR), * denotes outliers ± 3x IQR)

Copper

Unsurprisingly, copper roofs produced the highest concentration of total copper (mean and maximum of 1,663 µg/L and 7,860 µg/L, respectively), followed by asphalt road runoff with a mean of 29 µg/L and maximum of 84 µg/L, while galvanised and concrete roofs had similarly very low levels of total copper (<10 µg/L mean concentration). This clearly shows the scale of copper wash-off from the copper roof surface in stormwater runoff compared to any other single or combined source of copper (e.g. atmospheric deposition, vehicle brake pads). The copper roof mean concentration is higher by a factor of 57 and 166 from road and other non-copper roof surfaces, respectively.

Total copper concentrations for each surface were found to be significantly different from each other ($X^2(3) = 111.1$, $p < 0.001$), with a mean rank total copper concentration of 73.8 for concrete roof runoff, 146.7 for copper roof runoff, 40.0 for galvanised roof runoff and 103.7 for road runoff. Post hoc analysis identified statistically significant differences between all surface pairs expect for concrete roof and road.

Zinc

Similarly, the highest total zinc concentration was from the galvanised roof surface (mean and maximum of 397 µg/L and 1,970 µg/L), which most likely contributed direct dissolution of zinc. The road surface, with its multiple sources of zinc, had a higher mean zinc concentration (122 µg/L) compared to the two non-zinc roofs surfaces where only atmospherically-derived zinc was the likely source (16 and 39 µg/L for the concrete and copper roof, respectively). This represents a factor of 3, 10 and 25 higher mean total zinc concentration from a galvanised roof than from asphalt road, copper roof and concrete roof, respectively.

Total zinc concentrations for each surface were found to be significantly different from each other ($X^2(3) = 91.131$, $p < 0.001$). Post hoc analysis identified statistically significant differences between all surface pairs expect for concrete and copper roofs.

Lead

Lead concentrations were more similar for the four surfaces, with road runoff producing the highest mean concentration of total lead at 11.3 µg/L. The highest total lead value was measured from the copper roof at 107 µg/L, although the mean value was only 6.7 µg/L. Application of the Kruskal-Wallis test found that the total lead concentrations for each surface were found to be significantly different from each other ($X^2(3) = 52.9$, $p < 0.001$). Post hoc analysis identified statistically significant differences between all surface pairs except for concrete and copper roofs.

Total alkalinity

Elevated total alkalinity was observed for both concrete roof and asphalt road samples (Figure 4-2). This could be expected due to the calcium carbonate found in the cement used in the tiles on the roof and in the concrete kerb and channel along the road. The calcium carbonate leaches in the presence of acids in water.

The total alkalinity concentrations were higher for the concrete roof samples (mean of 28.6 mg/L as $CaCO_3$ and range of 9.3-52.7 mg/L as $CaCO_3$) than for the road runoff samples (mean of 13.7 mg/L as $CaCO_3$ and range of 1.9-30.6 mg/L as $CaCO_3$). Total alkalinity of untreated runoff is seldom reported, but the road runoff concentrations correspond to alkalinity reported in a study of carpark runoff by McQueen *et al.* (2010), which measured alkalinity ranging between <2-30 mg/L as $CaCO_3$. It is interesting to note that the concrete roof is at least 40 years old yet was still leaching a substantial level of alkalinity into the runoff, despite a significant period of time of exposure to the weather. The contribution of this alkalinity to the stormwater runoff could be expected to drive dissolved heavy metals in the runoff into particulate form, as metals precipitate out of solution at increased pH. Furthermore, increased hardness in the receiving waterway increases the Hardness Modified Trigger Values for heavy metal concentrations under instream water quality standards (refer to Chapter 2: Section 2.3.2), as the presence of calcium ions from the leached alkaline materials will compete with metal ions for surface binding on cells of aquatic organisms (Di Toro *et al.* 2001). Therefore the rate of bio-absorption of metals will likely be lower.

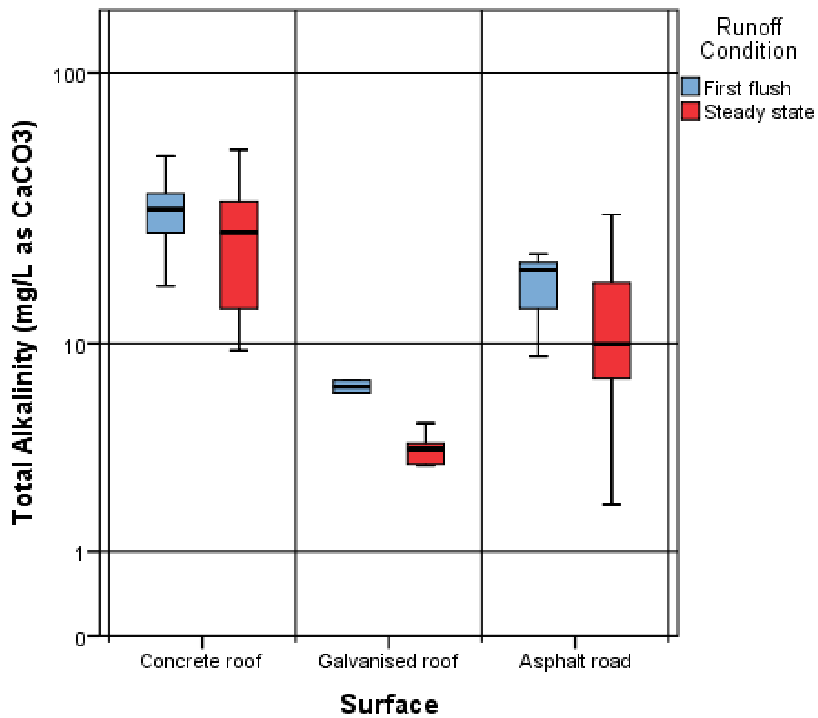


Figure 4-2: First flush and steady state total alkalinity

As a surface material with no expected source of alkalinity, some galvanised roof samples were also analysed for total alkalinity to quantify whether there is a noticeable contribution to total alkalinity from atmospherically deposited particles, especially given the likely presence of concrete dust particles in the local airshed due to post-earthquake demolition work. Total alkalinity concentrations were found, however to be not much greater than the analytical method's limits of detection (LOD of 2 mg/L as $CaCO_3$), and therefore total alkalinity analysis of galvanised roof runoff was discontinued and no total alkalinity analysis was undertaken of copper roof runoff.

4.3.3 Confirmation of first flush effect for TSS, Cu, Zn and Pb

Visual inspection of the distributions of initial to steady state concentrations for each surface (Figure 4-1) suggests that significant differences are probable for road runoff, copper and galvanised roofs for most of the TSS and heavy metal pollutants, but not for concrete roof runoff. This effect appeared even in the low intensity, short duration (and therefore small total rainfall depth) events.

Statistical analysis was therefore undertaken to further quantify the relationships for each of the TSS and heavy metal pollutants throughout the storm events (Table 4-6). As expected, initial TSS concentrations were found to be higher than the corresponding steady state concentrations to a statistically significant degree for road, copper roof and galvanised roof runoff, but not for the concrete roof data. However, for all three heavy metals, only galvanised roof runoff was found to have a statistically significant difference between initial and corresponding steady state concentration.

Table 4-6: Paired t-test for assessment of first flush presence

Surface type	Water quality parameter			
	TSS	**Total copper**	**Total zinc**	**Total lead**
Concrete roof	Mean diff = -0.46 t (7) = -0.092 p = 0.929	Mean diff = 0.57 t (6) = 2.034 p = 0.088	Mean diff = 0.00 t (6) = -0.001 p = 0.999	Mean diff = -1.49 t (6) = -0.485 p = 0.645
Copper roof	Mean diff = 1.27 t (3) = 5.565 p = 0.011 *	Mean diff = 0.16 t (4) = 0.786 p =0.476	Mean diff = 0.87 t (4) = 1.195 p =0.298	Mean diff = -0.02 t (4) = -0.028 p = 0.979
Galvanised roof	Mean diff = 1.59 t (8) = 4.966 p = 0.001 *	Mean diff = 0.57 t (8) = 4.282 p = 0.003 *	Mean diff = 0.96 t (8) = 3.906 p = 0.005 *	Mean diff = 0.73 t (8) = 3.806 p = 0.005 *
Asphalt road	Mean diff = 0.85 t (6) = 3.094 p =0.021 *	Mean diff = 0.23 t (4) = 0.987 p = 0.380	Mean diff = 0.46 t (4) = 1.441 p =0.223	Mean diff = 0.30 t (4) = 0.653 p = 0.550

***** Denotes statistically significant result. The significance level, p, is 0.05.

4.3.4 Transition time to steady state conditions

TSS and metal concentrations across first flush, transitional and steady state samples were compared against the time since the start of first flush to determine typical times to reach steady state conditions across the four sampled surfaces (Figure 4-3). For TSS, the roof surfaces showed similar trends to each other, with steady state conditions generally reached after 90 minutes. However, low concentrations for the copper and galvanized roof TSS shortly after the start of first flush demonstrates that the transition time varies widely between different rain events. Road runoff showed substantial variation in TSS concentrations over time.

Total copper and zinc transition times were relatively similar across the four surfaces, with steady state conditions generally reached after approximately 45 minutes. However, the transition trend for total lead was more similar to the TSS transition trend, with steady state conditions reached generally after 100 minutes.

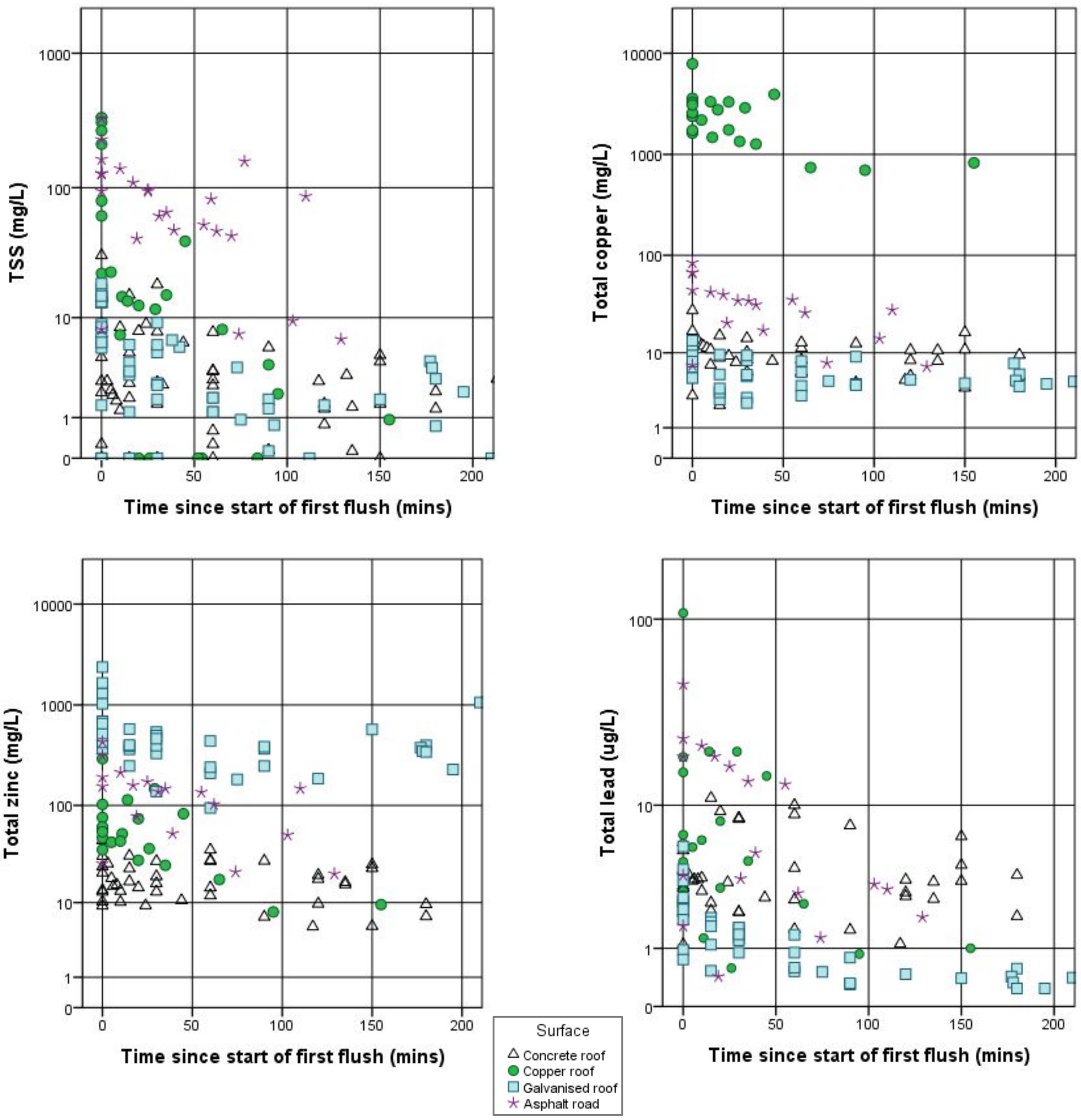


Figure 4-3: Transition time from first flush to steady state conditions for TSS and heavy metals

4.3.5 Comparison with international reported values

FF and SS mean concentrations for each surface in this study were compared with (untreated) runoff quality data collated from literature for various impermeable urban surface types to discern similarities or differences across different climates and regions (refer to Appendix A). The data was categorised by surface type into roof only, road only and mixed runoff, where multiple surfaces were contributing to the runoff. It should be noted that while the data was aggregated by surface type, the surface material may differ within each category (e.g. such as different roof types).

The mean TSS concentrations from this study were within the ranges reported elsewhere for the same surface type (Figure 4-4). However, both the FF and SS mean TSS for the road surface were lower than several reported Event Mean Concentrations (EMCs) for other locations. The FF and SS mean TSS for all three roofs (with the exception of the copper roof initial flush) were also substantially lower than most international reported roof EMCs yet similar to other New Zealand reported roof EMCs.

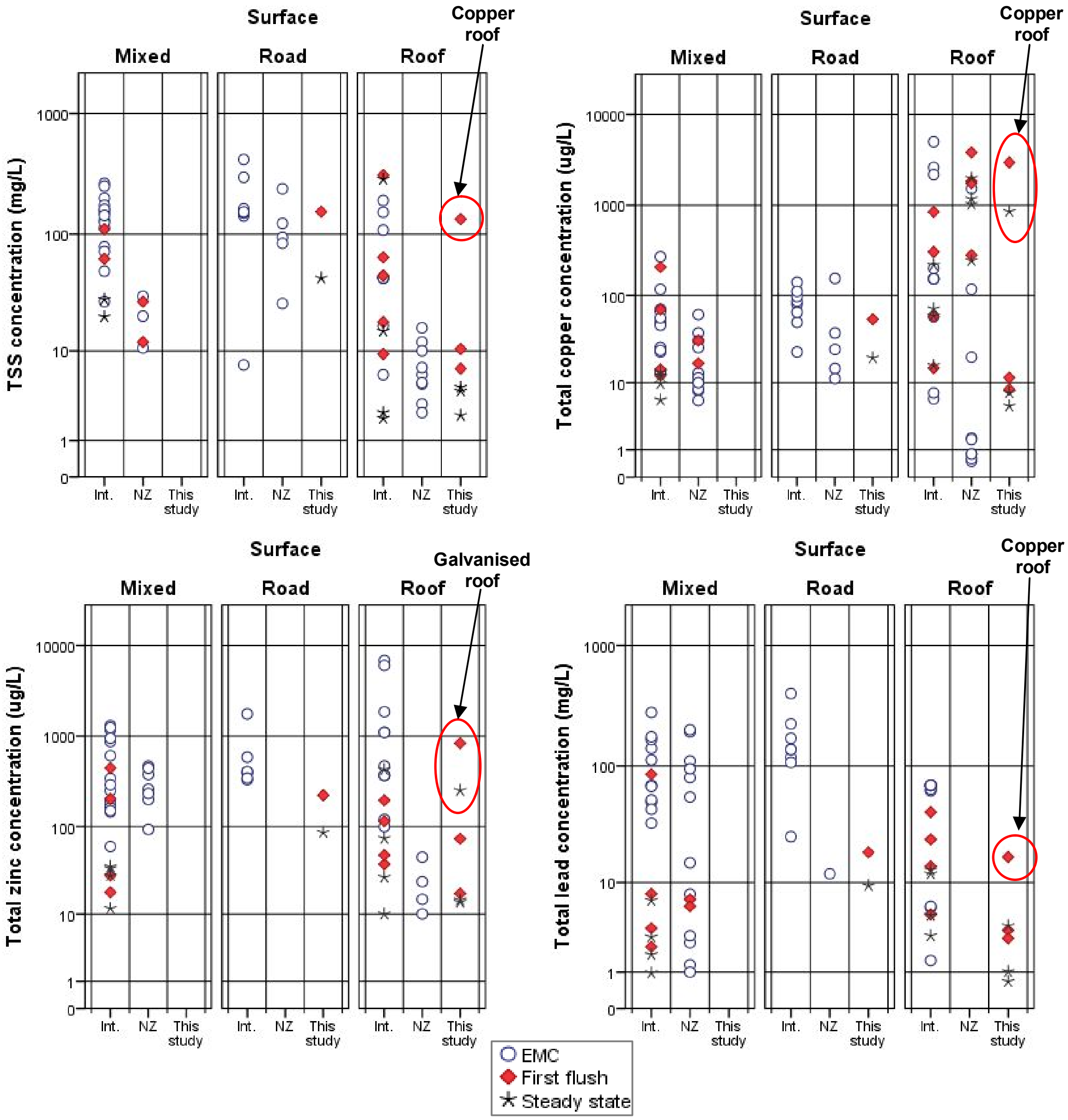


Figure 4-4: Comparison of this study's results against other New Zealand (NZ) and international (Int.) reported untreated runoff quality (refer to Appendix A for data sources)

FF and SS road mean total copper concentrations were lower than most international reported EMCs but similar to other New Zealand EMCs. The non-copper roofs were very low on a global scale, while this study's copper roof was similar to other copper roof reported elsewhere. This study's road mean total zinc values were lower than the limited number of reported international values; however, the galvanised roof values were higher than what has been previously reported in New Zealand studies, and sit at the higher end of the ranges reported internationally. The total lead concentrations for all four surfaces were at the low end of the range reported elsewhere with the exception of the copper roof initial mean concentration.

4.3.6 Heavy metal partitioning

Linear relationships between dissolved and total metal concentrations were generally consistent for both copper and zinc, with the exception of galvanised roof runoff for copper and concrete roof runoff for zinc (Figure 4-5), they show a consistent ratio. In contrast, lead relationships were widely scattered and concentrations were consistently low.

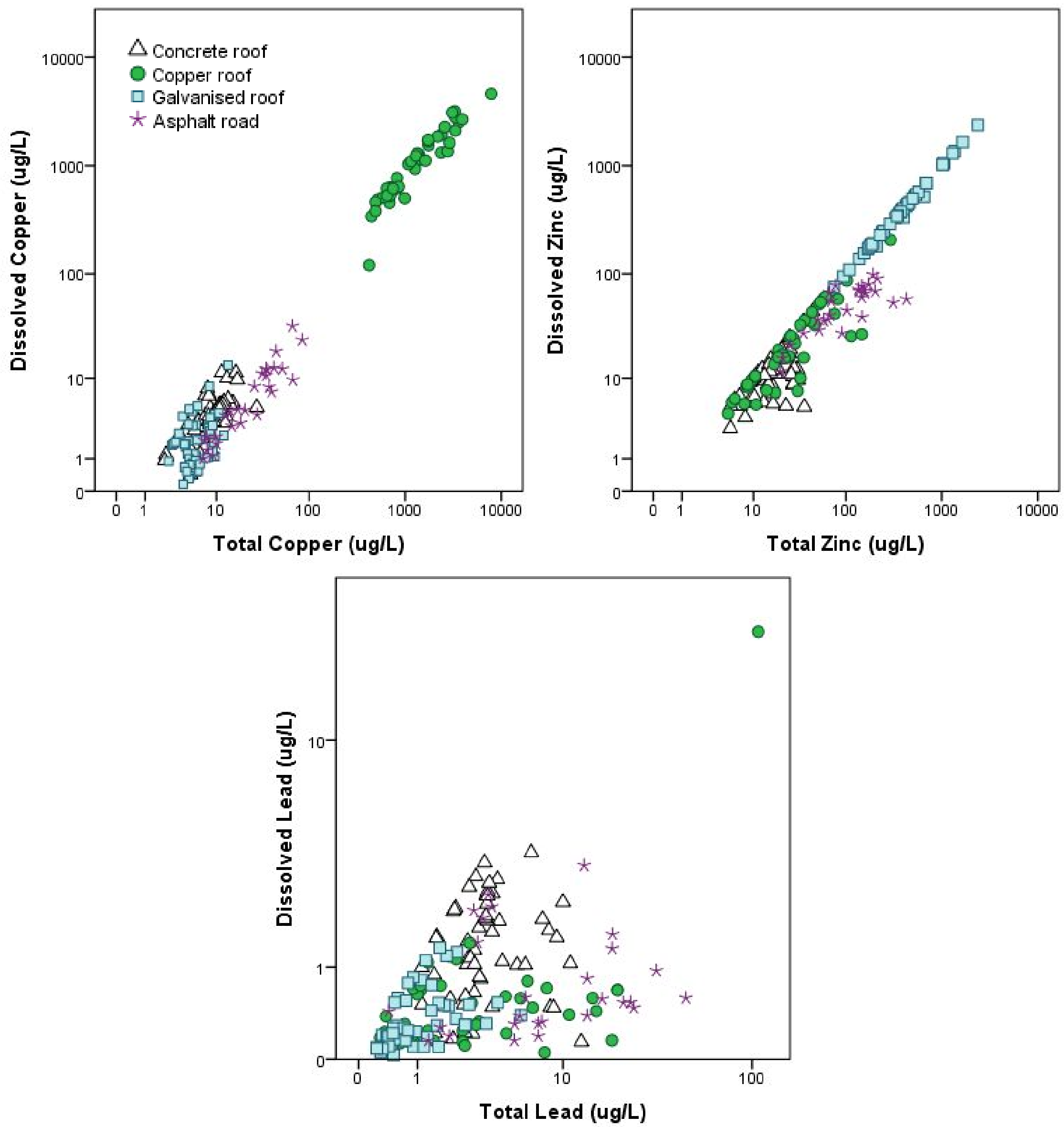


Figure 4-5: Total versus dissolved copper, zinc and lead concentrations

Strong positive correlations were found between total and dissolved copper and zinc concentrations for all four sampled surfaces (Table 4-7). The strongest correlations were confirmed, unsurprisingly for total and dissolved copper in the copper roof runoff and total and dissolved zinc in the galvanised roof runoff, indicative of metal dissolution processes being the key source of metal generation on these surfaces. For total and dissolved lead, only galvanised roof runoff was found to have a statistically significant correlation ($r = 0.591$, $p < 0.001$).

Table 4-7: Pearson correlation between total and dissolved metal concentrations

Surface Type	Copper	Zinc	Lead
Concrete roof	$r = 0.639$ $p < 0.0005$ *	$r = 0.633$ $p < 0.0005$ *	$r = 0.008$ $p = 0.956$
Copper roof	$r = 0.933$ $p < 0.0005$ *	$r = 0.691$ $p < 0.0005$ *	$r = 0.155$ $p = 0.328$
Galvanised roof	$r = 0.520$ $p < 0.0005$ *	$r = 0.999$ $p < 0.0005$ *	$r = 0.308$ $p = 0.031$ *
Asphalt road	$r = 0.864$ $p < 0.0005$ *	$r = 0.542$ $p = 0.004$ *	$r = -0.052$ $p = 0.798$

***** Denotes statistically significant result. The significance level is 0.05.

4.3.7 TSS as a predictor parameter for total metals

TSS was generally found to be an effective predictor parameter for all three heavy metals. Road runoff in particular showed strong correlations between TSS and all three metals, while copper roof and galvanised roof runoff also showed moderate to strong correlations for all three metals. The concrete roof runoff showed little correlation between TSS and metals, although lead was found to be an exception. Lead may be dissolved and released by lead-based fixtures and fittings in the guttering and adsorb to sediment being washed off from this roof.

Table 4-8: Pearson correlation between TSS and total metal concentrations

Surface Type	Correlation with TSS		
	Total copper	Total zinc	Total lead
Concrete roof	$r = -0.102$ $p = 0.464$	$r = 0.005$ $p = 0.969$	$r = 0.604$ $p < 0.0005$ *
Copper roof	$r = 0.483$ $p = 0.002$ *	$r = 0.502$ $p = 0.002$ *	$r = 0.425$ $p = 0.009$ *
Galvanised roof	$r = 0.586$ $p < 0.0005$ *	$r = 0.494$ $p < 0.0005$ *	$r = 0.751$ $p < 0.0005$ *
Asphalt road	$r = 0.903$ $p < 0.0005$ *	$r = 0.968$ $p < 0.0005$ *	$r = 0.860$ $p < 0.0005$ *

***** Denotes statistically significant result. The significance level is 0.05.

4.4 Discussion

4.4.1 TSS sources and wash-off behaviour

The four impermeable urban surfaces share atmospheric deposition from the Christchurch airshed as a source of sediment since they are located within the same catchment. Christchurch has a nearby source of wind-blown dispersive soils (loess) which may contribute to atmospherically-deposited TSS in Christchurch's airshed. However, the relatively low initial TSS concentrations washed off for concrete and galvanised roof runoff indicate that atmospheric deposition's contribution of sediment to urban runoff is actually low. The road surface has substantial sediment inputs from vehicle component wear and wash-off from car bodies that are absent from the other surfaces. This vehicular-derived sediment builds up during the antecedent dry period, but is also continuously contributed during the rain event from on-going vehicular activity, resulting in a higher steady state TSS concentration than other surfaces. The large difference between steady state roof and road TSS concentration further indicates that the intra-event contributions from vehicular activity are substantially larger than any contribution from atmospheric deposition. It is also likely that the process of pollutant wash-off from road surfaces are transport-limited where some but not all the particulates are washed off during a rain event, with more TSS carried over from one event to the next. This is probably due to the high degree of surface roughness facilitating temporary sediment storage within the interstitial spaces of the asphalt surface.

The differences in TSS behavior between the three roofs are most likely due to individual roof surface characteristics. The surface roughness influences the wash-off rate as sediment can be retained in interstitial spaces in coarse surfaces (i.e. the concrete roof, asphalt), while less energy (and therefore lower rainfall intensity) is required to entrain and mobilise sediment from smooth surfaces (i.e. the copper and galvanised roofs) (Pitt *et al.* 1995; Göbel *et al.* 2007). Surface slope and length also influence the wash-off rate by changing the runoff energy. The concrete roof and galvanised roof are a similar slope, however the copper roof is a combination of relatively flat areas with steepened sides. Surface orientation (aspect) also affects weathering rates by (prevailing) wind, rainfall, and solar radiation. The copper and concrete roof both face south to south-east, while the galvanised roof faces north (sunniest aspect in the southern hemisphere). However, it is likely that the majority of the differences in sediment concentrations between the impermeable surfaces are a direct result of the different surface material types.

The high initial TSS concentrations for the copper roof (compared to other roof surfaces) suggests that there is an additional source of fine particulate matter that is readily mobilized and washed off during the initial stages of the rain event. Visual inspections of the roof and guttering showed little to no vegetative debris, but the surface is covered with a green patina. The oxidation and degradation of the copper roofing material during dry periods between rain events (i.e. copper patination byproduct) is therefore considered to be a likely source of this additional fine sediment. The similarly smooth galvanised roof surface, which could be expected to have a similar wash-off rate as the copper roof, did not show elevated initial sediment levels indicative of any material flaking. The low steady state TSS concentrations in concrete, galvanised and copper roof runoff indicate that these surface material themselves are not significant sources of sediment during rainfall (note that the contribution of sediment due to copper patination is a dry weather process that is washed off during the initial stage of a rain event only). The wash-off process for TSS for all the roof surfaces is therefore likely to be source-limited, in that all available sediment is washed off during the course of the rain event, even in the low intensity rainfall conditions studied here. Other studies investigating wash-off sediment rates from roofs also found negligible amounts of TSS after the initial wash-off period (e.g. Mendez *et al.* (2011)).

4.4.2 Heavy metal sources and wash-off behaviour

Overall, road surfaces generally had higher concentrations of heavy metals than the roof surfaces, except where a metallic (e.g. Cu or Zn) roof surface contributed additional copper or zinc via direct dissolution from semi-acidic rainfall. In these cases, the copper roof produced over 50 times higher mean total copper concentration than the road surface, while the galvanised roof produced over 3 times higher mean total zinc concentration than the road surface. This metal dissolution process seems to result less from the influence of surface slope, orientation or roughness and more from the presence of these metals within the surface material itself. Accordingly, the inert concrete roof material showed negligible heavy metal generation. Similarly, galvanised roofs were a negligible contributor of total copper, while copper roofs contributed only very small concentrations of zinc.. Previous studies found average atmospheric deposition contributions of total copper in the range of 1-89 µg/L, total zinc in the range of 4-1,400 µg/L and total lead in the range of 0.5-580 µg/L (Murphy 2015). However, a recent study on atmospheric deposition contributions of heavy metals in urban runoff (Murphy, 2015) in the same catchment as this study, found concentrations at the low end of these ranges, with an average total copper concentration of 7.9 µg/L, total zinc load of 26.3 µg/L and total lead load of 2.2 µg/L, highlighting the small contribution of metals in urban runoff from atmospheric deposition within this catchment. The wash-off process for heavy metals from roads, copper from copper roofs and zinc from galvanised roofs is therefore likely to be transported-limited, as the high steady state concentrations demonstrate that these metals are still available on these surfaces even in the latter stages of a rain event, while the contribution of these metals from atmospheric deposition is likely to be source-limited.

Elevated lead concentrations were seen in initial copper roof runoff, coinciding with the elevated sediment concentrations, suggesting that lead-copper alloys (lead has historically been used as an alloy with copper for increased machinability) may be present in the roof fixtures (i.e. flashings) and the lead is being weathered and released as part of the patination process. A first flush effect for heavy metals was confirmed only for the galvanised roof surface. This is considered to be due to the complexity of pollutant build-up and wash-off processes on each surface. The galvanised roof is smooth and only has wash-off from atmospherically-deposited sediment (for copper and lead) and dissolution of roof material (for zinc). Conversely, while the copper roof is also a smooth metallic surface, copper originates from a combination of wash-off of copper patination material (dependent on the antecedent dry period), and copper dissolution during the rain event. The presence of copper patination material also likely attenuates atmospherically-deposited sediment containing any zinc and lead. The roughness of the concrete roof and road surfaces also likely attenuate the wash-off sediment associated with heavy metals, and will be influenced by the rainfall intensity throughout the rain event.

4.4.3 Implications for treatment approaches

Results from this study show that road surfaces provide the highest concentration of TSS under both initial and steady state conditions, however, copper roofs also provide elevated TSS concentrations during the initial period of rain, much of which is particulate copper. The low TSS in both concrete and galvanised roofs suggest individual treatment of these surface types for TSS is not essential. However, road runoff is often mixed in the kerb and channel with roof downpipe discharges and therefore becomes 'diluted' by the time it enters the stormwater discharge network. The amount to which it is diluted depends on the composition of the catchment that the kerb and channel serves; an area with substantial roof surfaces (e.g. residential or high-density commercial developments with undercover parking) could be expected to be substantially more dilute compared to untreated road runoff TSS concentrations, while a catchment with extensive hardstand areas (roads and carparks) will have higher concentrations of sediment in runoff. The diluted combined runoff would therefore require a larger capacity treatment system or more inlet flow attenuation due to its greater mixed volume. Therefore, interception of road runoff prior to it mixing in the kerb and channel may be warranted to reduce the 'treatable' volume. Systems such as median strip bioretention swales, tree pits and bioretention basins amongst parking spaces and other small-scale on-site systems intercepting runoff prior to reaching the kerb and channel are optimal where site conditions permit. Furthermore, studies have shown that stormwater treatment systems can achieve higher removal efficiencies for higher concentrated runoff (Lau & Stenstrom 2001; Strecker *et al.* 2001).

As the highest copper and zinc concentrations were consistently found from copper and galvanised roofs, respectively, and furthermore, were primarily in the more ecotoxic dissolved form, copper and unpainted galvanised roofs should be avoided or remediated to reduce the contribution of these heavy metals to urban waterways from untreated stormwater runoff. Road runoff treatment systems should also consider removal of both dissolved and particulate metals, as removal of particulate-associated metals via settling or filtration may not adequately reduce the overall metal loads in road runoff. Dissolved metals can be effectively treated in stormwater runoff provided a suitable treatment process is selected that facilitates processes of precipitation, sorption, filtration, or plant uptake and binding of the dissolved metals (LeFevre *et al.* 2014). Examples of systems that employ these processes include bioretention basins, carbonate/hydroxide dosing, wetlands (sulphide precipitation), proprietary organic/humic filters, gravel/rock biofilters and some engineered fabric filters. The performance of these systems varies with external factors such as temperature, runoff pH, and variations in redox conditions from fluctuations between wet and dry periods, and internal system factors such as media life expectancies, clogging and media cell structure (LeFevre *et al.* 2014).

The confirmation of a first flush effect for sediment, where initial peak concentrations were observed reducing thereafter to lower steady state concentrations, (even during rainfall events of low average intensity and low total rainfall depth), should be considered in design decisions for sizing first flush treatment systems. Commonly-used empirically based sizing approaches such as Schueler's (1987) method of treating the runoff volume produced by the first 25 mm of rainfall, or the State of California's (2001) definition of treating the runoff volume produced by the first 19 mm of rainfall, is overly conservative for low intensity rainfall events such as those in the studied catchment. In order to increase the efficiency of land footprints designated for stormwater treatment, an approach of targeting the initial peak sediment volumes rather than much larger (and typically combined) runoff volumes is recommended.

4.4.4 International context

The comparison of this study's results with other New Zealand and international studies highlights that the pollutant concentrations observed in Christchurch, under low rainfall intensity conditions, are typically at the low to medium end of the pollutant ranges observed elsewhere. The three key exceptions to this are: the high TSS initial copper roof runoff, the high total copper roof runoff during both initial and steady state stages, and the high total zinc from galvanised roofs during both initial and steady state stages. This suggests that the contribution of both atmospheric deposition and vehicle-related activities to sediment and heavy metal pollution in runoff is lower in Christchurch than overseas, but the contribution of heavy metals from metallic roof surfaces is comparable to international levels. The less-intensive industrial history, lower traffic densities and isolated geography combined with the lower intensity rainfall typically found in Christchurch may all influence this pattern. However, metals in runoff from direct dissolution of metallic roofs could be expected to vary with rainfall acidity; the rainfall pH recorded in this study is comparable to several New Zealand and international studies in urban areas of varying density and industrial history (Industrial: (Sequeira & Peart 1995; Zobrist *et al.* 2000; Karlen *et al.* 2002; Athanasiadis *et al.* 2007); New Zealand: (Fish 1976; Holden & Clarkson 1986; Pennington & Webster-Brown 2008).

There is significant variation in rainfall characteristics across the reported international studies, as would be expected from the global range of the studied sites. However, the focus of the comparison was to assess how a low intensity climate's stormwater runoff quality from common impervious surface materials compares to other urban areas around the world. This comparison helps guide stormwater management decision-making, for example, assessing what treatment performance could be expected in a low intensity rainfall climate from implementing treatment systems used elsewhere.

4.4.5 Implications for approaches to pollutant load modelling

Significant differences in pollutant concentrations for the four impermeable urban surfaces indicate that characterising the contribution from individual surfaces, as opposed to aggregation by land use or larger-scale features, is necessary for the development of an effective predictive pollutant load model. The strong associations identified between total and dissolved metals suggest total metal concentration may be an effective surrogate parameter to predict the more ecotoxic dissolved metal concentrations. Likewise, the strong association between total metal and TSS concentrations suggest TSS may be an effective predictor of total metal concentration for pollutant load modelling.

4.5 Conclusions

Significant differences were seen in both TSS and heavy metal concentrations in runoff from different impermeable urban surfaces. Road runoff should be targeted for sediment and heavy metals treatment, while copper and unpainted galvanised roofs should be avoided or remediated to reduce their high contribution of dissolved copper and zinc, respectively. Treatment strategies should aim to separate runoff sources for targeted treatment prior to mixing for the benefit of reducing treatment volumes and avoiding unnecessary treatment intensities and footprints.

Predictions of pollutant contribution from urban surfaces should consider the different surface materials. An aggregated land use approach may not adequately predict pollutant loads in catchments with copper and galvanised roofs in particular and consequently result in sub-optimal stormwater treatment designs or management approaches. TSS is likely to be an effective predictor variable for total metals, particularly for road runoff, while total metals themselves are likely to be effective predictor variables for dissolved metals for all four surface types, particularly for copper and zinc.

In cities like Christchurch where low rainfall intensity and short duration storms occurs, road runoff was seen to be a transported-limited process for TSS, with carryover of sediment likely occurring between rain events. However, TSS runoff from the metallic roof surfaces appears to be source-limited even with the low rainfall intensity. Heavy metal generation in both road and metallic roof surfaces were seen to be transport-limited processes as concentrations remained high during steady state conditions.

5 Particle Size Characteristics of Untreated Urban Runoff

5.1 Introduction

This chapter outlines the characterisation of particle size distributions (PSDs) of sediment in the untreated runoff from the four impervious urban surfaces in the Okeover catchment. The key aims of this section of the research are:

1. Identify typical particle size distributions for first flush and steady state conditions for each sampled surface type,
2. Assess whether there are significant differences in key PSD metrics between first flush (FF) and steady state (SS) samples,
3. Assess whether differences in PSD during a rain event (intra-event variation) or across several rain events (inter-event variation) are statistically significant and should be accounted for in management decision-making and design,
4. Compare this study's results to other international studies of urban runoff PSDs to provide context for future PSD studies, and
5. Describe the implications of the PSDs on stormwater treatment selection, design criteria and expected performance.

5.2 Background

5.2.1 Variation in PSD

Only a limited number of studies have examined variations in PSDs from a single site either during individual rain events (intra-event variation) or across multiple rain events (inter-event variation). A study by Furumai *et al.* (2002) of the wash-off behavior of different particle size fractions in highway runoff observed a stepwise relationship in TSS wash-off under varying natural runoff conditions, attributed to different wash-off behavior of finer versus coarser particles. Muthukaruppan *et al.* (2003) analysed particle size composition of road surface runoff and concluded that underlying catchment geology impacted the PSD, while minimal inter-event variation was observed in each catchment. Further studies by Brodie and Dunn (2009), Selbig and Bannerman (2011) and Selbig (2013) compared PSDs from various urban surfaces across multiple events using flow-weighted composite samples (i.e. inter-event variation analysis only).

Particle wash-off behavior and particle settling rates both vary in relation to particle size (Brodie & Dunn 2009).Understanding variation in PSD in runoff from a surface therefore provides an indication of the likely variation in treatment performance that can be achieved by various sediment removal treatment systems. This variation can be considered a performance risk, if the treatment system is not designed to settle or filter particles over the majority of the size fractions that are present in the runoff.

5.2.2 PSD effects on treatment selection and performance

Sediment treatment processes include physical filtration, sedimentation (settling) and enhanced sedimentation via chemical coagulation/flocculation (Clark & Pitt 2012). However, the design and performance of these treatment systems are sensitive to many factors, particularly the concentration and particle size composition of the sediment in the untreated runoff, as the capability of the treatment unit varies across particle size fractions. For example, PSD characterization is considered an important aspect of wet pond design, as particle settling velocity influences the pond size (Greb & Bannerman 1997). A review of published literature and technical manuals showed that while many documented overall TSS removal efficiencies, treatment performance was not typically quantified in terms of percent removal for individual particle size fractions. Ferreira and Stenstrom (2013) reported on the theoretical and experimentally-measured TSS removal by a hydrodynamic separator and a dry detention basin, and the Toronto Region and Conservation Authority (2002) reported on experimentally-measured TSS removal achieved in a 151,000 m^3 pond and wetland system treating runoff from a 600 ha residential catchment.

Variations in the influent PSDs both during and over multiple rain events present an additional uncertainty that can influence the overall performance of the treatment system. Studies to date on PSD intra-event variability consider only single site road runoff, and inter-event variability studies considered only event mean PSDs. Particle size composition and its variability across multiple surface types for the same rainfall conditions need to be examined to enable robust runoff quality modelling and targeted treatment system selection.

5.3 Methodology overview

A full description of the sampling sites, sampling techniques used, lab analysis and data analysis is provided in Chapter 3. An overview of the pertinent aspects of the methods used to generate and analyse the PSD datasets discussed in this chapter is provided here:

Runoff samples were collected from 15 rainfall events from four impermeable surfaces within the Okeover Stream catchment (a mixed residential/institutional land use catchment). The four sites were in close proximity of each other (within 320 m) such that they were considered to have been exposed to the same climate characteristics, including antecedent dry period and rainfall conditions for each sampled event.

A combination of grab sampling and automatic sampling (ISCO 6712C Compact Portable Automatic Sampler) was used to capture untreated runoff during first flush (FF; defined as the first 2 L of runoff), transitional and steady state (SS) conditions. Samples were analysed for TSS and PSDs. The samples were analysed as non-dispersed samples as this is considered to represent how sediment would aggregate and be transported under natural runoff conditions (Slattery & Burt 1997).

Christchurch has a nearby source of wind-blown dispersive soils (loess) which may contribute to atmospherically-deposited TSS in Christchurch's airshed. To enable comparison of this source material to mixed composition runoff, a sample of loess material taken from a hill site facing the city (8.1 km SE of the study area) was also analysed for PSD using the same PSD analyser settings.

Average and 5-minute peak rainfall intensity, event duration and length of the antecedent dry period were recorded for each event using a University weather station adjacent to the copper roof site. This data was compared against meteorological records from the National Institute of Water and Atmosphere's (NIWA) Weather Station, 2.2 km from the sampling sites, and found to be similar and therefore representative of rainfall conditions for the wider Christchurch. The NIWA station data was used when the University weather station data was not available for maintenance reasons.

5.3.1 Review and compilation of published PSD data

International peer-reviewed literature was reviewed from which PSD data in untreated urban runoff was compiled from all urban surface types. PSDs derived from street sediment (i.e. vacuum samples direct from a dry street surface) were included for general comparison, although it is recognized that particle aggregation may occur in such sediments and therefore not provide a necessarily representative PSD for sediment entrained in runoff (Slattery & Burt 1997).

5.3.2 Rainfall characteristics

Samples were obtained from 15 rainfall events between March to June 2014 (i.e. autumn to early winter) and October 2014 to March 2015 (i.e. spring to mid-summer). Due to the different runoff characteristics of each surface type and sampling logistics, not all surfaces could be sampled for every event, however there were six sampling events where all four surfaces were sampled concurrently. Average rainfall intensity ranged from 0.2 mm/hr to 4.8 mm/hr, with a median value of 1.4 mm/hr, while peak 5-minute rainfall intensity ranged from 1.6 to 16.8 mm/hr (median of 2.4 mm/hr). Event duration ranged from 0.3 to 31 hours and total rainfall depth ranged from 0.4 to 144 mm. One sampled event on 4 March 2014 had a depth of 144 mm and an average intensity of 4.8 mm/hr which exceeded the 5% annual exceedance probability (AEP) for a rainfall event in the catchment, as predicted by the High Intensity Rainfall Design System Version 3 (HIRDS.V3) (NIWA 2011). The length of antecedent dry period ranged from 4.3 hours to 13.5 days (median of 3.6 days). The depth of the immediately preceding rain event ranged between 0.4 mm to 143.8 mm (median of 1.2 mm).

Table 5-1: Sampling event characteristics

Event no.	Date	Rainfall pH	Average intensity (mm/hr)	Antecedent dry days (days)	Event duration (hrs)	Total depth (mm)	Depth of previous event (mm)
1	4 Mar 2014	6.35	4.8	0.6	30	144	0.4
2	16 Mar 2014	6.38	3.0	10.5	16	41	144
3	5 May 2014	6.01	1.6	5.6	0.3	0.4	1.8
4	8 May 2014	5.93	0.7	3.3	5.7	3.6	0.4
5	26 May 2014	5.86	2.4	0.6	4.9	5.2	1.4
6	6 Jun 2014	6.26	0.3	0.3	1.3	0.4	0.6
7	9 Jun 2014	5.82	1.4	0.2	31	43	1.2
8	16 Jun 2014	5.46	2.4	3.5	0.3	0.8	16
9 *	25 Jun 2014	5.81	1.5	7.2	1.1	1.6	5.8
10 *	3 Oct 2014	5.74	2.0	5.4	1.1	2.2	0.4
11	18 Oct 2014	5.10	1.0	8.9	1.2	1.2	1.2
12 *	22 Nov 2014	5.67	0.5	2.8	2.4	1.3	4.4
13 *	10 Dec 2014	5.93	0.8	0.2	1.3	1.0	1.2
14 *	9 Feb 2015	6.31	0.9	3.6	0.7	0.6	4.4
15 *	6 Mar 2015	6.05	1.4	3.2	4.3	6.0	0.8

* indicates all four surface sampled for that particular rain event

5.3.3 Statistical analysis

Statistics were conducted using R (Release 3.1.3) statistical software (R Core Development Group 2015). Key metrics used in statistical analysis were D_{50} (i.e. median particle size), D_{10} and D_{90} (i.e. the size at which 10% and 90% of particles pass, respectively) and the percentage of fine particles (<63 µm). D_{10} and D_{90} are representative of outlying size classes, and the percentage of fine particles (<63 µm) represents the divide between clay/silt particles and sand/gravel particles as per ISO 14688 International Soil Classification. Furumai et al. (2002) noted evidence of different wash-off behavior between fine and coarse particles, and therefore this is considered an important metric for analysis of temporal and surface differences.

Intra-event variation was analysed by paired sample t-tests between FF and SS PSD metrics for each rain event, for each surface type. There were a minimum of 6 rain events for each surface type where first flush and steady state samples were collected. By the time of the later storm events, the time to steady state (under a variety of rainfall conditions) was well understood based on more intensive intra-event sampling in earlier events. Therefore, for some of the later rain events, only a first flush sample and one steady state sample were taken, with the steady state sample taken at a time when the surface runoff had been previously observed to remain in steady state conditions. Analysis of the sample for TSS concentration was also used as a further means of confirming that the sample was taken during steady state conditions (i.e. there was little change in TSS concentration).

As a measure of the differences between each surface, independent t-tests were conducted for all key PSD metrics as well as TSS concentrations. Welch's versions of the t-tests were selected as equal variance could not be assumed for the dataset. Correlation analysis, using Pearson's, was conducted between PSD metrics and various rainfall characteristics across all sampled events (inter-event variation). The criterion used for statistical significance (*p* values) was 5%. Appendix F provides a summary of the dataset size and composition for each of the statistical tests undertaken.

5.4 Results

5.4.1 Review of literature-reported PSDs

A summary of published PSD studies is presented in Table 5-2, with corresponding PSDs as a function of impermeable surface category, presented in Figure 5-1. The figure shows the percentage of sediment passing (y-axis) each particle size fraction (x-axis). The data show distinct ranges of PSDs for both highway and car park runoff, while urban road runoff varies most widely of any runoff type. An original representative PSD for mixed use runoff (i.e. combined runoff from several surfaces) was developed under the United States National Urban Runoff Program (NURP), which sought to characterize urban runoff quality aspects across different urban sites (Driscoll 1986). The value is mass-based using data from multiple sites across the US. However, it is considerably finer than any of the reported highway, road or carpark PSDs. Later mixed runoff studies showed a wide range of PSDs, as would be expected from the diversity of surfaces that contribute to a mixed runoff sample. While few studies have characterised roof PSDs, Brodie and Dunn (2009) reported a roof PSD that was comparable to road and carpark runoff PSDs, while a multi-surface study by Selbig and Bannerman (2011) found similar roof and feeder road PSDs.

Table 5-2: Studies of urban runoff and sediment PSDs with median particle size (modified from Selbig (2013))

Study	Sample Type	*Code* [1]	Runoff Type	Catchment description	Estimated D_{50} (μm) [2, 3]	PSD analysis method
Sartor and Boyd (1972)	Grab samples	*1*	Urban road – multiple sites	Street dust from 10 cities across US	320 *	Unspecified, reported % by weight
Shaheen (1975)	Grab samples	*2*	Highway sediment	Single site; drainage area unspecified; concrete surfaced; 73,000 vehicles/day	207 *	Wet sieved to 75 μm
Driscoll (1986)	Event Mean	*3*	Mixed runoff [3]	Multiple sites; developed for National Urban Runoff Program (NURP)	8	Settling tests
Greb and Bannerman (1997)	Event Mean	--	Mixed runoff	Single site; predominantly residential catchment; 0.96 km^2 drainage area	<4	Settling tests
Sansalone *et al.* (1998)	Intra-event samples (FF and SS), Event Mean	*4*	Highway runoff	Single site; 300 m^2 drainage area; asphalt surfaced; interstate	570 *	Particle analyser
Furumai *et al.* (2002)	Intra-event samples (FF)	--	Highway runoff, dust and sediment	Single site; 8.4 ha urban highway catchment; asphalt surfaced highway	<50 *	Wet sieve to 20 μm
Li *et al.* (2005)	Intra-event samples (FF and SS)	--	Highway runoff	Three sites: 0.39–1.69 ha, surface not specified, all sites >260,000 vehicles/day	2.7 – 7.1 *	Particle analyser
Zanders (2005)	Grab samples	*5*	Urban road sediment	Single site: 60.7m long concrete kerb adjacent to asphalt road, ~25,000 vehicles/day	250 *	Sieve analysis
Anta *et al.* (2007)	Intra-event samples (FF and SS); Event Mean	*6*	Mixed runoff	Single site; residential-commercial catchment; 39,000 m^2 drainage area; typically tiled roofs and asphalted roads	38	Particle analyser
Kim and Sansalone (2008)	Event Mean	*7*	Highway runoff	Single site; two adjacent 544 m^2 drainage areas; concrete surfaced; interstate	136 *	Wet sieved to 75 μm; particle analyser
Brodie and Dunn (2009)	Event Mean	*8*	Urban road runoff	Single site; 450 m^2 drainage area; asphalt surfaced; 3,500 vehicles/day	26 *	Wet sieving and filtration to 8 μm
		9	Carpark runoff	Single site; 56 m^2 drainage area; concrete surfaced	33 *	
		10	Roof runoff	Single site; 52 m^2 drainage area; galvanised	23 *	

Study	Sample Type	*Code* [1]	Runoff Type	Catchment description	Estimated D_{50} (μm) [2, 3]	PSD analysis method
Selbig and Bannerman (2011)	Event Mean	*11*	Urban road (feeder) runoff	Single site; 1,620 m^2 drainage area; asphalt surfaced; <1,500 vehicles/day	200 *	Wet sieved to 32 μm; particle analyser to 2 μm
		12	Urban road (arterial) runoff	Single site; 9,190 m^2 drainage area; concrete surfaced; 40,000 vehicles/day	95 *	
		13	Urban road (collector) runoff	Single site; 3,760 m^2 drainage area; asphalt surfaced; 10,000 -15,000 vehicles/day	70 *	
		14	Carpark runoff	Three sites: A - 1.3 ha drainage area, B – 2.4 ha, C – 0.4 ha; all asphalt surfaced	54 *	
		15	Mixed runoff	Single site; 1.1 ha drainage area; mixed land use	42 *	
		16	Roof runoff	Single site; commercial land use; 290 m^2 drainage area; flat, rubber surfaced	95 *	
Moores *et al.* (2012)	Event Mean	--	Carpark runoff	Single site; commercial land use; 0.45 ha drainage area	63-125	Particle analyser
	Event Mean	--	Road runoff	Single site; arterial road; 0.98 ha drainage area	63-125	
	Event Mean	--	Road runoff	Single site; highway bridge deck; 859 m^2 drainage area	31-63	
Selbig (2013)	Event Mean	*17*	Urban road (feeder) runoff	Data combined from two study sites; 1,619 m^2 and 2,833 m^2 drainage area; asphalt surfaced	50 *	Wet sieved to 32 μm; particle analyser to 2 μm
		18	Urban road (arterial) runoff	Data combined from two study sites; 9,186 m^2 and 8,498 m^2 drainage areas; one concrete, one asphalt-surfaced	43 *	
		19	Urban road (collector) runoff	Single site; 5,665 m^2 drainage area; asphalt surfaced	8 *	
		20	Carpark runoff	Single site; 23,876 m^2 drainage area; asphalt surfaced	32 *	
		21	Mixed runoff	Single site; 11,169 m^2 drainage area	95 *	
		22	Residential runoff	Single site; 212,458 m^2 drainage area	80 *	

Study	Sample Type	*Code* [1]	Runoff Type	Catchment description	Estimated D_{50} (μm) [2, 3]	PSD analysis method
This study	Intra-event samples (FF and SS)	--	Roof runoff	Single site; concrete tile	81	Particle analyser
		--	Roof runoff	Single site; galvanised	61	
		--	Roof runoff	Single site; copper	72	
		--	Road runoff	Single site; asphalt surfaced; 11,000 vehicles/day	71	

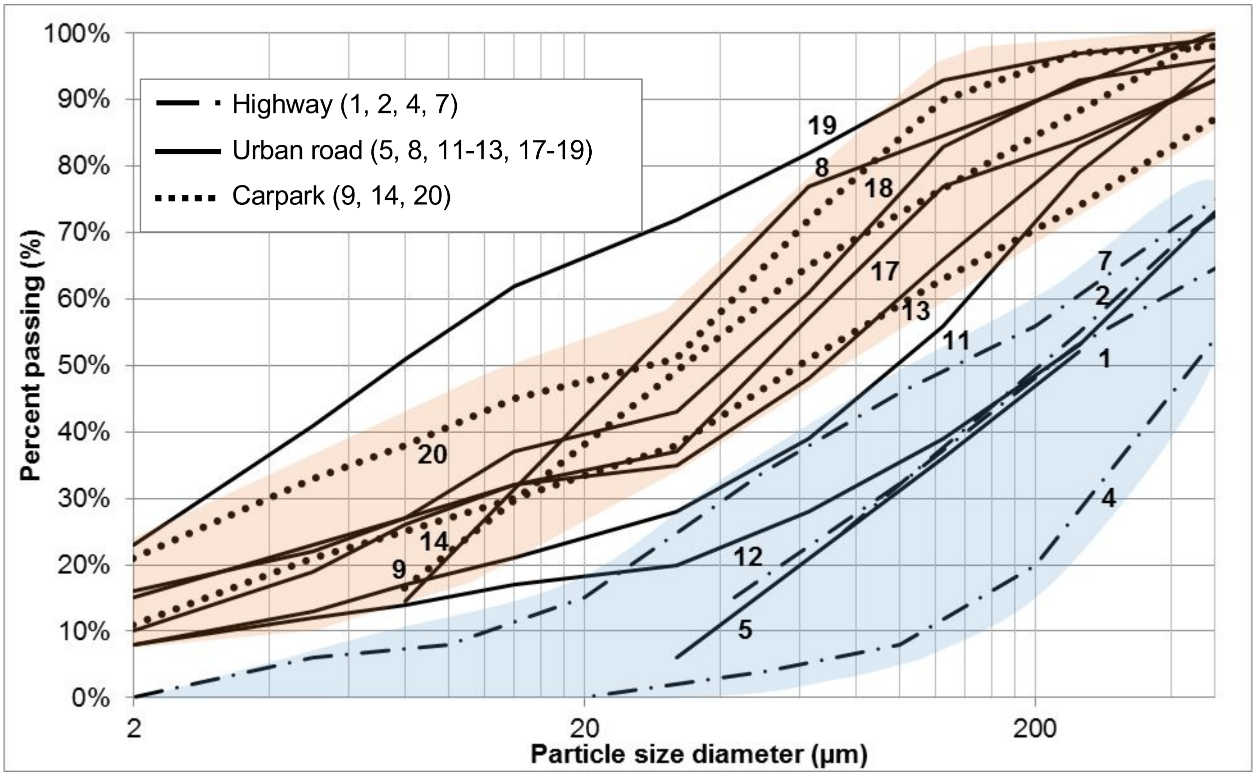
[1] Unique identifier corresponding to PSD shown in Figure 5-1

[2] Exponential interpolation used to estimate D_{50} from described PSD where D_{50} not explicitly stated

[3] D_{50} is volumetric median size unless noted

[4] Mixed runoff contributed from multiple surfaces of different types

* Weight-based median size



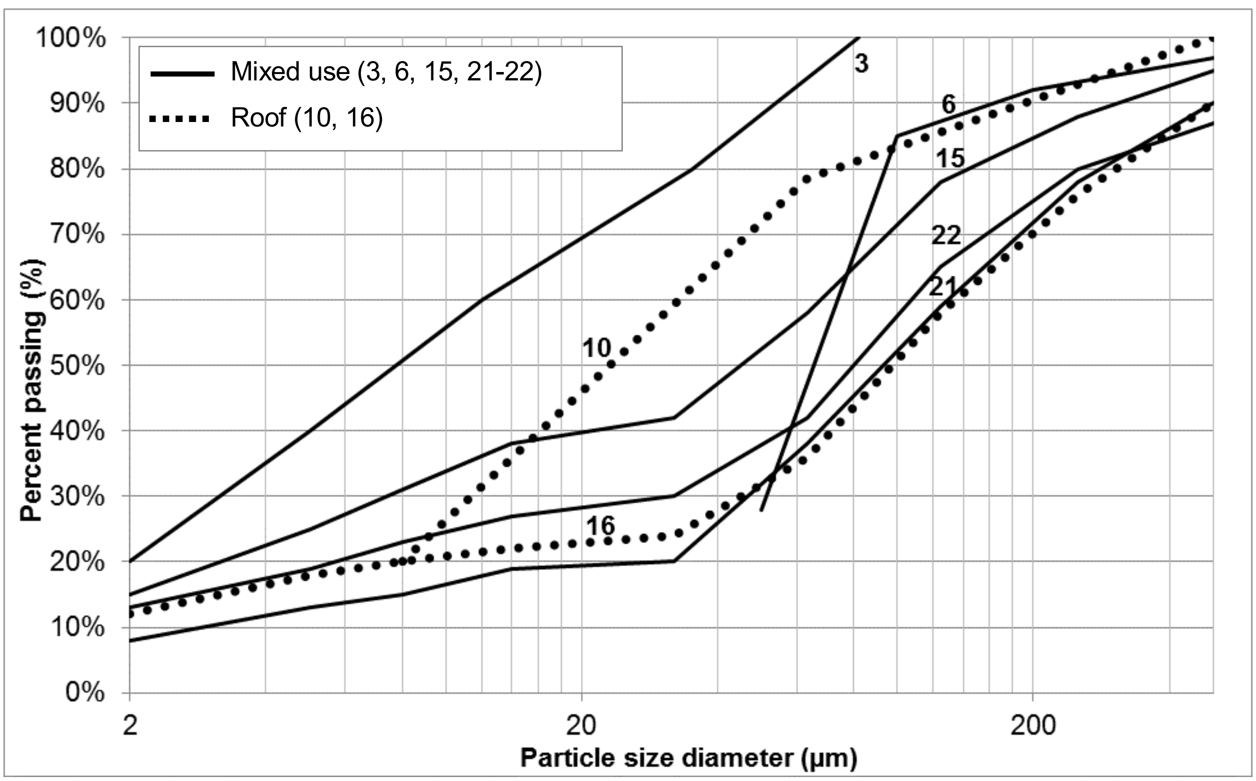


Figure 5-1: Runoff PSDs from different urban surfaces (Top: Highway, urban roads and carparks; Bottom: Roofs and mixed catchments) (Data sourced from Table 5-2 references)

5.4.2 Typical PSDs for each surface type

Typical PSD profiles for the Okeover study area were developed for each surface type, based on the mean value for each size fraction from all PSDs for that surface. Asphalt road runoff was found to have a bi-modal distribution, with consistent peaks centred around 6-10 and 70-100 μm (Figure 5-3). A notable but very minor peak was also seen in 5 of the 8 sampled rain events centred around 0.2-0.4 μm. Individual road PSDs contributing to the typical PSD profile were inspected to confirm whether the bimodal distribution observed was the result of bimodal distribution in all samples or of two distinct monomodal distributions. All individual road PSDs were bimodal. Galvanised roof runoff PSDs had a more unimodal distribution, centred at 60-100 μm with a very minor peak around 10 μm. Like road runoff, a minor peak was also seen in some of the sampled events at 0.3 μm. Copper roof runoff showed the highest variation in PSDs across all samples, and could be generally described as having a unimodal distribution centred around 60-90 μm, a clear minor peak at 10-15 μm and a likely minor peak around 150-200 μm that is partly masked by the primary peak. Concrete roof runoff PSDs had a clear major peak at 70-90 μm and a minor peak at 10-12 μm was observed in four of the sampled events. The loess sample showed a major peak at 60 μm with a low shoulder from 20-60 μm (Figure 5-3).

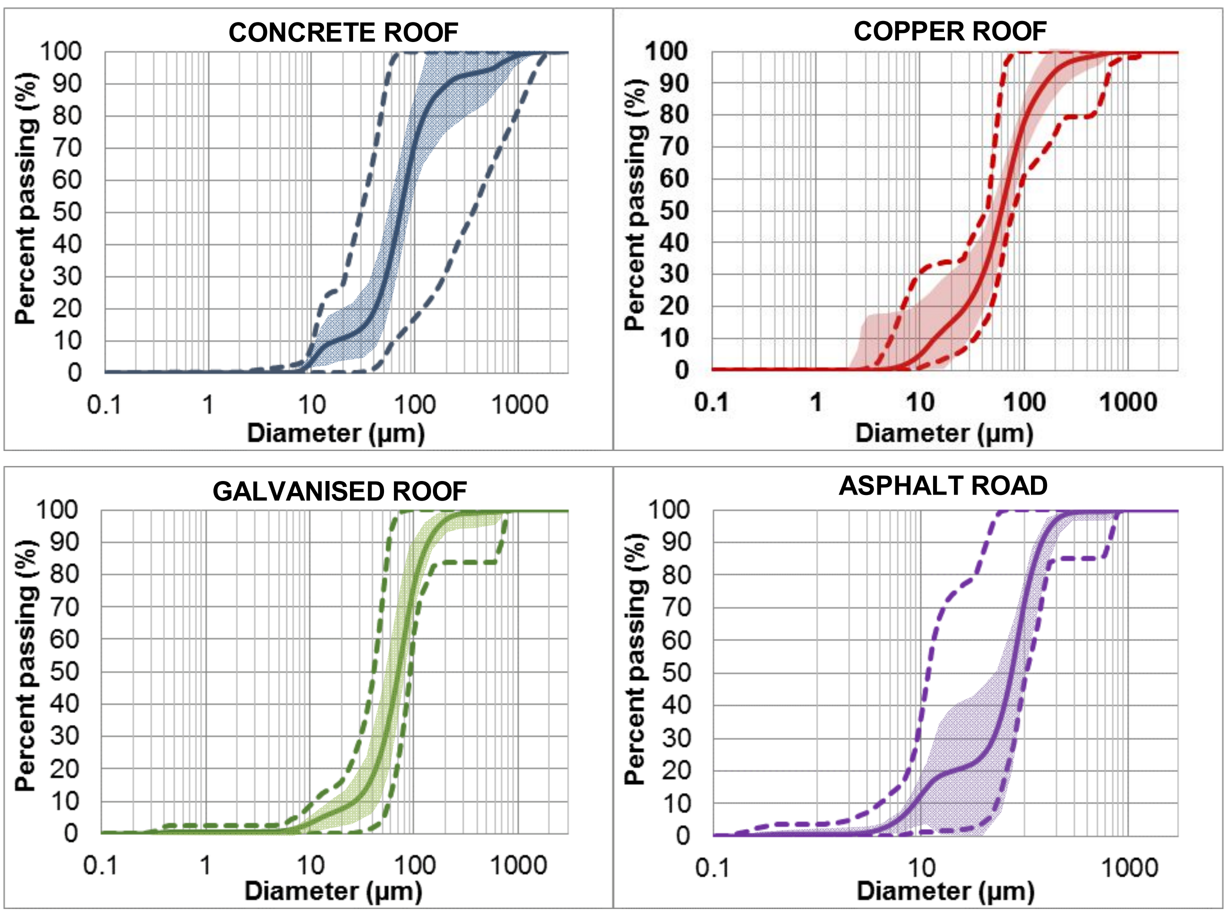


Figure 5-2: Mean cumulative PSDs (solid lines) ± 1 S.D. (shaded area) and observed ranges (dotted lines) for the four surface types

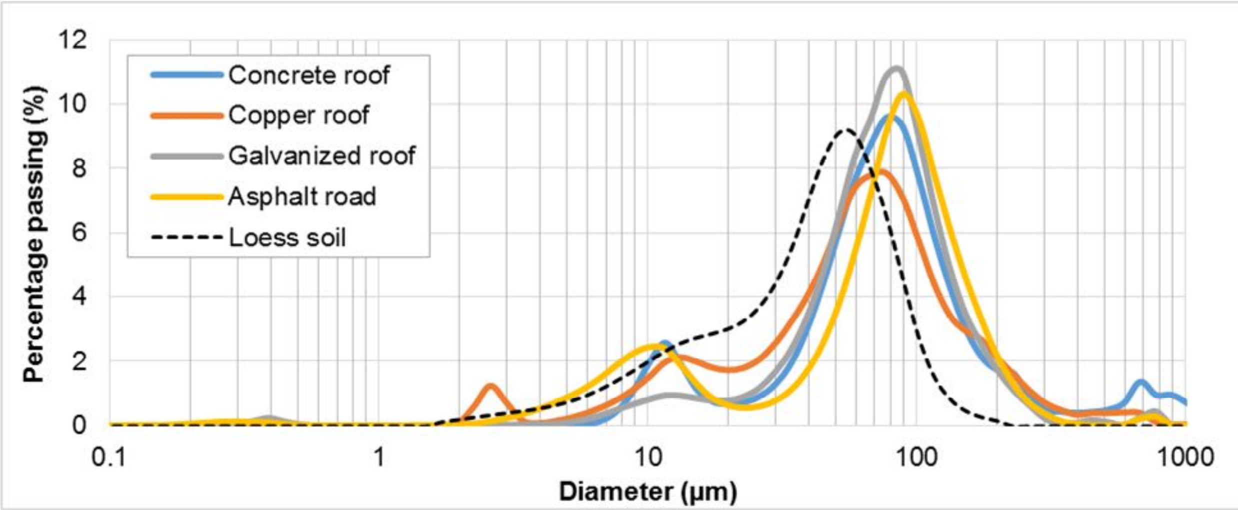


Figure 5-3: Mean frequency PSD for the four surface types compared to mean loess soil PSD

The percentage of particles that are <63 µm (classified as fine sediment) was also analysed for each surface, with considerable variation for all surfaces (Table 5-3). Road runoff had the highest variation in fine sediment ranging from 3 to 100% sediment being <63 µm, followed by concrete roof runoff (14 to 98%) and galvanised roof runoff (14 to 95%), with the copper roof runoff having a distinctly smaller range (37 to 92%). Furthermore, if variation in the entire PSD is assessed (Figure 5-2), it is clear that asphalt road and concrete roof runoff PSDs vary most widely across most class sizes as they have the largest observed ranges.

Table 5-3: Summary statistics for typical PSDs for roof and road runoff (mean, with range in brackets)

Runoff Type	No. of samples (*n*)	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)	Percentage of fines (% <63 µm)
Concrete roof	27	24.7 (10.3 – 58.1)	71.0 (29.9 – 96.7)	276.9 (53.2 - 976.3)	41.8 (14.0 – 97.7)
Copper roof	25	18.1 (5.3 – 33.9)	60.8 (43.2 – 78.3)	162.2 (61.0 – 398.7)	53.8 (36.7 – 91.8)
Galvanised roof	23	30.3 (10.9 – 57.9)	72.1 (52.8 – 91.5)	164.5 (75.1 – 683.4)	41.0 (13.87 – 95.3)
Asphalt road	28	23.2 (4.0 – 53.7)	71.6 (11.7 – 102.9)	177.2 (42.4 – 784.5)	38.9 (3.0 – 99.8)

5.4.3 Intra-event variation

Limited variation was observed between first flush (FF) and steady state (SS) samples of the same event. Four of the nine sampled events of the concrete roof runoff showed a more centralized major peak for SS samples than the FF sample for the same event, meaning the finest particles (e.g. <20 μm) and the coarsest particles (e.g. >200 μm) were mostly washed off during the initial stages of each rain event (Figure 5-4). However, this phenomenon was not consistently seen across all concrete roof events and a statistical analysis of all samples did not indicate that this was significant. The other surfaces did not show any clear trends, with high variability amongst both FF and SS samples.

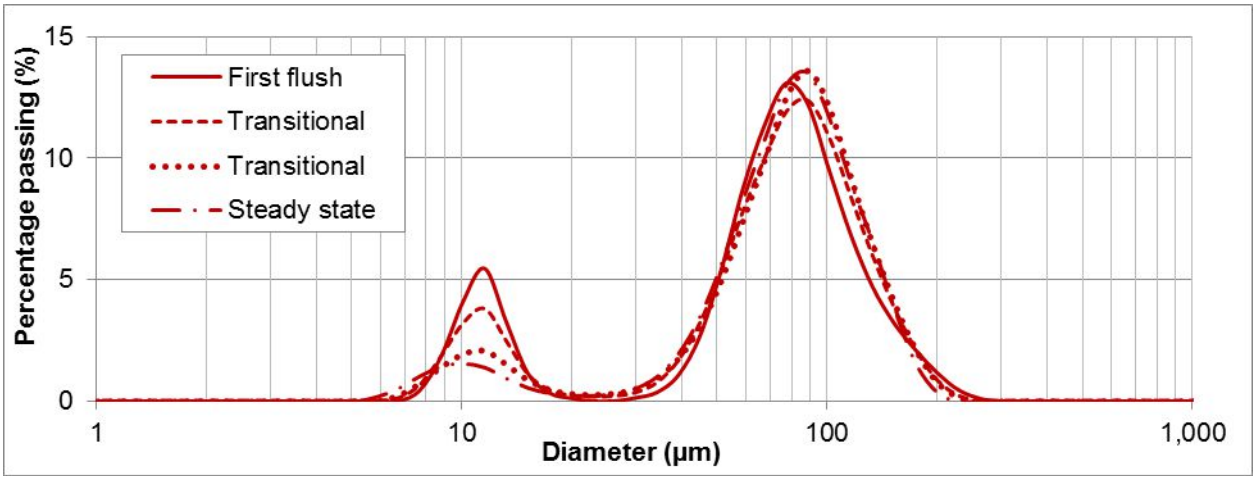


Figure 5-4: Concrete roof runoff (Event 9) showing PSD change from FF to SS conditions

Paired t-tests did not show any statistically significant differences between FF and SS values for the same event, for D_{10}, D_{50}, D_{90} or percentage of fines for any surface. Therefore, for further inter-event and runoff type comparisons, the full dataset was used (i.e. FF, transitional and SS samples) in all statistical analyses.

5.4.4 PSD comparisons between surfaces

t-tests between each surface type indicated that concrete and copper roof runoff varied to a statistically significant level for D_{50} ($t(47) = 3.18$, $p < 0.05$), D_{90} ($t(31) = 2.07$, $p < 0.05$) and percentage of fines ($t(47) = -3.04$, $p < 0.05$). Similarly, copper roof runoff varied significantly from galvanised roof runoff for D_{10} ($t(33) = -3.51$, $p < 0.05$), D_{50} ($t(41) = -3.45$, $p < 0.05$) and percentage of fines ($t(36) = 2.74$, $p < 0.05$). Copper roof runoff also varied significantly from road runoff for D_{50} ($t(35) = -2.11$, $p < 0.05$) and percentage of fines ($t(42) = 3.02$, $p < 0.05$). There were no significant differences between road runoff and either concrete roof or galvanised roof runoff, nor between concrete roof and galvanised roof runoff.

5.4.5 Inter-event variation

Analysis of PSD metrics against key rainfall characteristics showed that only galvanised roof and asphalt road runoff were significantly (and moderately) correlated to rainfall characteristics for D_{10} values (Table 5-4). For D_{50} values, concrete roof and road runoff were the only surfaces significantly correlated, while for D_{90} values, only copper roof runoff showed any significant correlation. Correlations for the percentage of fines closely resembled inverse D_{50} correlations, as the 63 μm threshold values were very similar to the D_{50} values for concrete roof, galvanised roof and road runoff. However, other correlations between fines and total event duration and depth were found for the copper roof runoff. All significant correlations were moderate to strong.

PSD metrics from road runoff had the strongest correlations to rainfall characteristics (Table 5-4). It was found to correlate with both average and peak intensity, rainfall pH, event duration and depth. Concrete runoff also correlated well with peak intensity, event duration and depth, and with the depth of preceding rain event and the cumulative depth at the time the sample was taken. None of the surfaces showed a statistically significant correlation with antecedent dry period.

Table 5-4: Correlation analysis between key PSD metrics and rainfall characteristics

Runoff Type	Correlations with D_{10}	Correlations with D_{50}	Correlations with D_{90}	Correlations with percentage of fines
Concrete roof		INTpk (*r*= -0.55, p<0.01) Dur (*r*= -0.44, p<0.05) DEPt (*r*= -0.53, p<0.01) DEPp (*r*= -0.60, p<0.01) DEPs (*r*= -0.60, p<0.01)		INTpk (*r*= 0.59, p<0.01) Dur (*r*= 0.43, p<0.05) DEPt (*r*= 0.52, p<0.01) DEPp (*r*= 0.67, p<0.01) DEPs (*r*= 0.66, p<0.01)
Copper roof			pH (*r*= 0.44, p<0.05) DEPp (*r*= 0.57, p<0.01) DEPs (*r*= 0.57, p<0.01)	Dur (*r*= 0.47, p<0.05) DEPt (*r*= 0.42, p<0.05)
Galvanised roof	pH (*r*= -0.47, p<0.05) INTavg (*r*= -0.42, p<0.05) INTpk (*r*= -0.47, p<0.05)			
Asphalt road	INTavg (*r*= -0.43, p<0.05) INTpk (*r*= -0.43, p<0.05) Dur (*r*= -0.44, p<0.05)	pH (*r*= -0.41, p<0.05) INTavg (*r*= -0.78, p<0.01) INTpk (*r*= -0.79, p<0.01) Dur (*r*= -0.66, p<0.01) DEPt (*r*= -0.85, p<0.01)		pH (*r*= -0.45, p<0.05) INTavg (*r*= 0.78, p<0.01) INTpk (*r*= 0.81, p<0.01) Dur (*r*= 0.68, p<0.01) DEPt (*r*= 0.84, p<0.01)

INTavg = average intensity ($mm.hr^{-1}$); INTpk = peak intensity ($mm.hr^{-1}$); Dur = duration (hrs); DEPt = total depth of sampled event (mm); DEPp = depth of previous rain event (mm); DEPs = cumulative depth at time of sample (mm)

5.4.6 Total suspended solids

Total suspended solids data was analysed for only the samples for which PSD analysis had also been done (i.e. using a truncated TSS dataset from 15 rain events instead of the 24 rain events used for the full TSS and metals dataset, as was analysed in Chapter 4). This was done to enable comparison between PSD metrics and TSS for the same sample set.

Untreated road runoff was generally found to have an order of magnitude higher TSS concentrations than any of the roof surfaces for both FF and SS flow under the same rainfall conditions (Table 5-5). The copper roof was also found to have very high FF TSS, even though its SS results were similar to concrete and galvanised roofs.

Table 5-5: Range of TSS concentrations for each surface type

Surface Type	First flush			Steady state		
	Mean (mg/L)	Minimum (mg/L)	Maximum (mg/L)	Mean (mg/L)	Minimum (mg/L)	Maximum (mg/L)
Concrete roof	11.9	2.7	30.8	4.1	2.5	7.6
Copper roof	191.5	13.9	453.7	3.3	1.2	11.7
Galvanised roof	13.4	6.2	22.3	4.0	1.2	6.8
Asphalt road	158.2	77.1	327.4	53.5	16.4	157.2

Independent t-tests between each surface type indicated that concrete roof TSS was significantly different from copper roof runoff ($t(32) = -2.19$, $p<0.05$) and road runoff ($t(26) = -5.14$, $p<0.01$) but not to galvanised runoff. Likewise, galvanised roof runoff was different to a statistically significant level to copper roof runoff ($t(32) = -2.25$, $p<0.05$) and road runoff ($t(26) = -5.23$, $p<0.01$). First flush copper roof and road TSS concentrations were not shown to be significantly different from each other, but there were differences in steady state concentrations.

5.4.7 Review of treatment performance variation by particle size class

The overall TSS removal for the asphalt road PSDs (i.e. minimum, mean and maximum PSDs) was calculated based on the reported percent removed for different size fractions by three different treatment systems (Table 5-6). As the treatment systems generally remove more of the coarser size fractions, it follows that the maximum PSD profile (i.e. the profile derived from the maximum cumulative distribution value for each size fraction) will achieve the greatest treatment, as it has the highest proportion of sediment in the coarser size fractions. Likewise, the minimum PSD profile represents the finest PSD derived from the samples and accordingly will achieve the lowest overall TSS removal.

The reported experimental removal rates of a hydrodynamic separator indicated that the unit was most effective at removing coarse particles (58 to 100% for particles >250 µm) and not at all effective at removing particles <70 µm (Ferreira & Stenstrom 2013). In contrast, both the dry detention basin (Ferreira & Stenstrom 2013) and pond and wetland system (Toronto Region and Conservation Authority 2002), while also using settling as the primary mechanism to remove sediment, provided much longer hydraulic retention time and therefore enabled finer sediment as well as the coarser sediment to settle out within the treatment system.

Table 5-6: Predicted range in treatment performance (% removal) for measured range of asphalt road PSDs

Treatment system	Reference	Particle size range (µm)	Percentage removal (%) [Min.-max.; mean]	Measured road PSDs (% frequency in each size range)			Predicted treatment performance (overall percent TSS removal by size fraction)		
				Mean	Finest	Coarsest	Mean	Finest	Coarsest
Hydrodynamic separator (experimental performance)	Ferreira and Stenstrom (2013)	<70	0%	49	100	23	0	0	0
		70 – 150	19 – 21%	43	--	54	8 – 9	0	10 – 11
		150 – 250	41 – 69%	6.7	--	7.7	3 – 5	0	3 – 5
		250 – 425	58 – 87%	0.6	--	--	0 – 1	0	0
		>425	95 – 100%	0.7	--	15	1	0	14 – 15
						Total TSS Removal (%)	***12 – 15***	***0***	***28 – 32***
Dry detention basin	Ferreira and Stenstrom (2013)	<8	57 – 75%	9.2	23	0.8	5 – 7	13 – 17	1
		8 – 20	84 – 91%	12	51	1.1	10 – 11	43 – 47	1
		20 – 100	84 – 95%	52	26	46	44 – 50	22 – 25	39 – 44
		>100	100% [1]	27	--	52	27	0	52
						Total TSS Removal (%)	***87 - 95***	***78 - 88***	***92 - 97***
Pond and wetland	Toronto Region and Conservation Authority (2002)	<2	84%	0.7	3.5	--	1	0	0
		2 – 63	96%	42	96	17	40	93	16
		63 – 2,000	100%	58	0.2	83	57	0	83
		>2,000	100%	--	--	--	0	0	0
						Total TSS Removal (%)	***97***	***93***	***99***

[1] Treatment of particles >100 µm not specified, assumed 100% removal

The results show that the overall performance of the hydrodynamic separator could range from 0 to 32% TSS removal, combining both the variation in the treatment unit capability and the variation in the influent PSD. This is a wide range in TSS removal and also highlights the possibility of no TSS removal occurring in these types of treatment devices with a fine influent PSD and a lower hydraulic retention time (HRT). The dry detention basin and pond and wetland systems, both with a longer HRT, provided a narrower range of TSS removal as they were capable of removing a wider size range of particles. The treatment range, considering worst case influent characteristics and system performance, is calculated at 78 to 97% TSS removal for the dry detention basin, and 93 to 99% for the pond and wetland system.

5.5 Discussion

5.5.1 Sediment sources

All four impermeable urban surfaces shared a common particle size peak of around 60 – 100 µm and had a similar PSD profile. The similarity of the loess PSD to these suggests that loess may be a particular contributor to runoff sediment through atmospheric deposition in the study catchment. This potential influence of local soil type has been previously observed by Muthukaruppan *et al.* (2003), where a catchment within sedimentary geology was found to generate coarser sediment than another catchment in the same city but within basaltic geology. However, further studies into individual source PSDs as well as a greater number of samples is required to confirm the key sources of sediment to runoff in this catchment.

The road runoff PSDs with a peak of around 6-10 µm was not seen for any of the other surfaces, suggesting this material could be derived from degradation of vehicle components such as tyres and brake linings. This is comparable with the findings of Cadle and Williams (1978) that stated that wear-emitted tyre particles typically range from 0.01 to 30 µm. Copper roof runoff had unique peaks around 10-20 µm, which may result from surface corrosion particles unique to the copper surface. However, there is little research on the size of particles derived from copper corrosion, and further work is required to confirm this.

5.5.2 Comparison of this study to other studies

While there will be differences in PSD results depending on both the measurement method used (Eshel *et al.* 2004) and potential biases in sampling (e.g. the tendency of autosamplers to collect a higher proportion of fines), it is still useful to make a general comparison between reported PSDs including our study's data. All roof runoff PSDs in our study had fewer fine particles (≤20 µm) and fewer very coarse particles (>200 µm) than other roof PSDs (Brodie & Dunn 2009; Selbig & Bannerman 2011), but a higher percentage of particles between 40 and 200 µm than other roof PSDs. Likewise, the road runoff PSD showed fewer particles sized ≤10 µm than other studies, but a higher percentage in the range 50 to 200 µm. This may be due to factors such as the less intense industrial history of Christchurch compared to other international cities, lower traffic density generating vehicle-related sediment or the specific contribution of loess to the PSD within Christchurch's airshed.

In general, all four surfaces from this study show a stronger 'centralising tendency' (i.e. less evenly distributed across particle size fractions) than seen in other studies, suggesting there is a local source of sediment which dominates the particle contribution in this catchment. In particular, the NURP PSD that is also adopted in Auckland, New Zealand, is significantly finer than any of the four surfaces sampled in this Christchurch study, highlighting the importance of characterising local sediment runoff for optimal selection of a sediment removal system. Sediment removal treatment devices are generally most effective at removing coarser particles, unless a long retention time can be provided such as in a large pond or wetland system. Treatment performances reported internationally could thus be expected to be readily achieved under local Christchurch conditions, based on this study's measured PSDs indicating a higher relative proportion of coarser sediments.

5.5.3 Implications of total suspended solids results

While the four surfaces studied were all likely influenced to some degree by the same atmospheric deposition as a source of sediment, the road surface has additional sediment inputs from vehicle component wear and wash off from car bodies, contributing to the higher TSS concentration. It is also possible that the sediment built up on the surface during dry periods between rain events is of the magnitude that it cannot be readily entrained and transported within the initial rain period (i.e. the first flush period for the road surface is extended as the available sediment initially exceeds the wash off and carrying capacity of the rain). The high copper first flush TSS suggests there is an additional source of fine material that is readily mobilized and washed off during the initial stages of the rain event, considered to likely be degradation of the copper roofing material during the dry periods between rain events.

5.5.4 Implications of variations on treatment selection and performance

Substantial differences in FF and SS PSDs signatures indicate that different treatment mechanisms may be needed to achieve effective sediment removal throughout a rain event. The lack of consistent intra-event variation suggests that there is little need to consider separate first flush and steady state treatment approaches for this catchment. Further research is needed in other catchments to quantify potential differences in intra-event variation.

5.6 Conclusions

Previous studies that analysed multiple surface types within the same catchment showed substantial diversity in PSDs, with highway and higher-trafficked urban roads having the coarsest PSDs, and carparks and mixed use runoff having the finest PSDs. However, this study's analysis of untreated runoff PSDs from a concrete roof, copper roof, galvanised roof and asphalt road surface within the same catchment showed similar PSD form and similar median (D_{50}) values. This suggests a shared sediment source (e.g. atmospherically-deposited loess) could be influencing the PSD on all four surfaces. Other major findings from this study's data include:

1. SS road runoff TSS was an order of magnitude higher than any roof runoff. FF road and copper roof runoff were both at least an order of magnitude higher than that from concrete roof and galvanised roof runoff. Road runoff should be targeted for TSS removal.
2. This study's PSDs were more concentrated around a peak particle size between 60 – 100 µm and had less fines than PSDs reported elsewhere for the same runoff type.
3. Concrete roof and asphalt road runoff, in particular, had substantial variation in PSDs across all samples from each of those surfaces.
4. While FF effects were observed in TSS during a single rain event, limited intra-event variation was observed between FF and SS PSDs. This indicates that separate FF and SS sediment removal approaches are unlikely to be required.
5. Inter-event variation was observed for all surfaces. However, significant correlations between PSD metrics and rainfall characteristics were primarily seen in concrete roof and asphalt road runoff.

The wide range in PSD from this study's surfaces, particularly the road surface with its high overall TSS, means that smaller 'on-site scale' treatment devices such as hydrodynamic separators carry a high performance risk of not being able to achieve adequate TSS removal across all rain events. While treatment systems with significant retention times such as wetlands enables settling of the finer sediments, these are typically only feasible for centralised systems where runoff is collected from a large catchment area. Source reduction and on-site treatment approaches may be desirable to minimize or treat other pollutants being carried in the runoff. This reinforces the need for a treatment train approach that combines these on-site and larger scale systems to provide a comprehensive management approach to the range of pollutants within runoff.

6 Development and Application of Pollutant Load Model Framework

6.1 Introduction

This chapter outlines the process used to develop a new model framework (MEDUSA: Modelled Estimates of Discharges for Urban Stormwater Assessments), calibrate MEDUSA to local Christchurch (low intensity) rainfall conditions and apply it to an initial case study catchment.

As outlined in Chapter 2: Section 2.5.4, current available pollutant load models have various limitations that restrict their ability to provide guidance at a fine spatial scale of the pollutant loads generated within a catchment. Such detail enables stormwater managers to develop effective, targeted strategies for improving stormwater quality and thereby reducing its adverse effects on the receiving urban waterways. Existing models are typically: annual load models; models that aggregate the contribution of runoff from individual surfaces by land use or subcatchment; models that typically predict total metal loads only (and not dissolved and particulate fractions); or models which require an extensive monitoring dataset to calibrate and run.

MEDUSA is a surface-scale pollutant load model that is intended to improve on available models to enable stormwater managers to develop effective, targeted strategies for improving stormwater quality and thereby reducing its adverse effect on the receiving urban waterways. It is a discrete, event-based model (a single load output per modelled event, for individually delineated roof, road and carpark surfaces); it simulates the build-up and wash-off processes of stormwater pollutants on those individual impermeable surfaces. It predicts TSS and total and dissolved copper and zinc load contributions from each surface for a single rain event (Figure 6-1). The model uses GIS mapping to represent each contributing surface within the catchment and assign the surface with properties such as its area (m^2), surface material, and which discharge point into the waterway the surface is connected to via the surface water drainage network. It then uses numerical modelling to calculate the expected pollutant load per surface based on the surface attributes assigned in GIS and the rainfall characteristics of the storm event being modelled (specifically, rainfall pH, average event intensity (mm/hr), number of antecedent dry days (days) and event duration (hrs)). While pollutant loads are calculated for a single rainfall event, they can be summed to provide seasonal or annual load estimates. The model outputs can be reported as maps of average event loads or per area loads. The outputs can also be tabulated to describe, for example, the comparative loads contributed by different surface types or the range of loads predicted to be generated by a surface over several rain events.

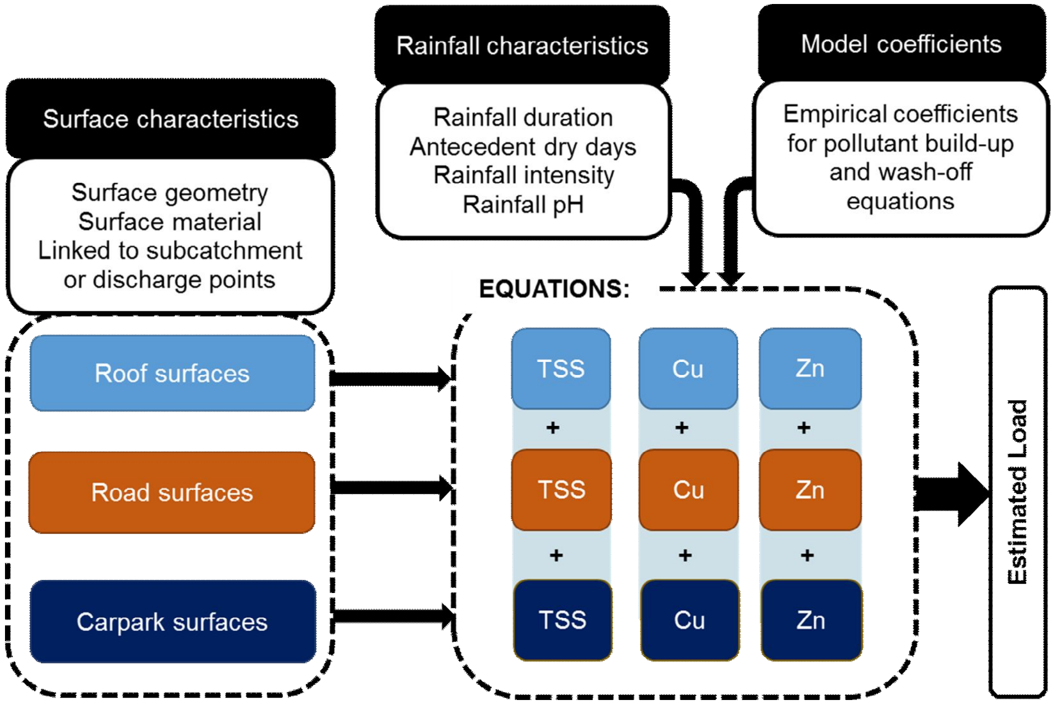


Figure 6-1: MEDUSA model framework (modified from Fraga *et al.* (2016))

The prediction of pollutant loads from individual surfaces for a single rain event assists stormwater management decision-making in several ways:

- The highest load-generating surfaces can be identified and targeted for stormwater management
- The predicted load characteristics (i.e. how much and, for metals, whether in particulate or dissolved form) can be used to select and size an appropriate treatment system
- The predicted loads can inform Total Maximum Daily Load limits by predicting at-source pollutant generation to be accounted for in the predictions of the pollutant load and pollutant form that reaches the receiving waterway (refer to Chapter 2: Section 2.3.1)

MEDUSA can also be run for multiple rain events to simulate seasonal and annual loads. These loads signify the potential cumulative or chronic effect of the pollutants on the receiving environment. The incorporation of GIS mapping in the model framework allows clear presentation of the spatial distribution of pollutant loads as well as communicating the model outputs to stormwater managers and decision-makers.

The model framework aims to:

- Recognise the different pollutant build-up and wash-off processes (for different surface types and materials, as well as in different rainfall climates);
- Provide a robust prediction of pollutant load while requiring only a limited monitoring dataset for calibration that is practical for stormwater managers to collect (without overly compromising model performance); and

- Provide a methodology for incorporating other pollutants of concern (e.g. other heavy metals, nutrients) in the future

6.2 Development of MEDUSA model framework

6.2.1 Selection of modelled pollutants

The MEDUSA framework is able to model various metals, however, copper, lead and zinc have previously been identified as the primary metals of concerns in New Zealand urban waterways (Auckland Regional Council 1992a; Zanders 2005; Brown & Peake 2006; Auckland Regional Council 2010b). Lead was observed during the untreated runoff sampling programme to be at low levels in the runoff and therefore has not been included in the model as runoff is not likely to be a major source of any elevated lead levels in the receiving environment (i.e. it is more likely a legacy issue of historically higher lead levels bound in stream bed sediments, for example). Sediment was also selected for the initial development and application of this model as it is considered to be a key stressor in urban aquatic systems and can be a key transport mechanism that carries heavy metals into urban waterways.

6.2.2 Representing TSS build-up and wash-off on urban surfaces

Overview

Sediment builds up on urban surfaces during the dry period between rain events as a result of atmospheric dry deposition, direct deposition from vehicles and degradation of the surface material itself (refer to Chapter 2, Section 2.2.2). Some further sediment is contributed during the rain event via wet deposition, where the raindrops scavenge particles from the air as they fall (Sabin *et al.* 2005), via dissolution of the surface material due to acidity of the rainfall (Quek & Förster 1993; Wicke *et al.* 2014) or from ongoing direct deposition from vehicles. During rain events, kinetic energy in the raindrops enables the entrainment and transportation of pollutants from the impermeable surfaces (i.e. pollutant wash-off).

Roof surfaces

MEDUSA uses an exponential decay relationship that relates the amount of pollutant built up prior to the start of the rain event, the pollutant wash-off rate and rainfall characteristics, to calculate the amount of material, w_t (g), washed off a roof surface during a single rain event (Egodawatta *et al.* 2009):

$$w_t = w_0.Area.C_f(1 - e^{-k.INT.DUR}) \quad (6\text{-}1)$$

where	w_0	Initial mass per unit area of material on roof surface (i.e. at t = 0)	(g/m^2)
	$Area$	Area of contributing roof surface	(m^2)
	C_f	Capacity factor (ability of intensity to mobilise particles)	(dimensionless)
	k	Wash-off coefficient	(mm^{-1})
	INT	Rainfall intensity	(mm/hr)
	DUR	Duration of rain event	(hours)

The use of a first order decay relationship to describe wash off was originally developed by Sartor and Boyd (1972); Egodawatta et al (2009)'s more recent work updates the relationship with a capacity factor, C_f, that describes how the rain's ability to mobilise particles changes with intensity. Egodawatta *et al.* (2009) also observed a power relationship between pollutant build-up , w_0, and the number of antecedent dry days, ADD:

$$w_0 = a_1 . ADD^{a_2} \tag{6-2}$$

where	a_1	Linear coefficient	(g/m^2/day)
	a_2	Exponential coefficient	(dimensionless)
	ADD	Number of antecedent dry days	(days)

The capacity factor from Eqn. 6-1, Cf, for roof runoff was found by Egodawatta *et al.* (2009) to have a step-wise relationship with rainfall intensity, INT:

$$C_f = \begin{cases} 0.75 & \rightarrow INT < 20\ mm/hr \\ a_3 . INT + a_4 & \rightarrow 20 \leq INT < 40\ mm/hr \\ 0.91 & \rightarrow 40 \leq INT < 90\ mm/hr \\ a_5 . INT + a_6 & \rightarrow 90 \leq INT < 115\ mm/hr \\ 1.0 & \rightarrow INT \geq 115\ mm/hr \end{cases} \tag{6-3}$$

where	a_3, a_5	Linear coefficients	(dimensionless)
	a_4, a_6	Constants	(dimensionless)

The wash-off coefficient, k, is a constant value, relating the rate of exponential decay in the TSS concentration to each surface type.

By substituting Eqns. 6-2 and 6-3 into Eqn. 6-1, the resulting MEDUSA model equations for the amount of TSS (g) contributed from roof surfaces become:

$$TSS_{Roof} = \begin{cases} a_1 . ADD^{a_2} . Area . (0.75) . \left(1 - e^{(-k.INT.DUR)}\right) & \rightarrow I < 20\ mm/hr \\ a_1 . ADD^{a_2} . Area . (a_3 . INT + a_4) . \left(1 - e^{(-k.INT.DUR)}\right) & \rightarrow 20 \leq I < 40\ mm/hr \\ a_1 . ADD^{a_2} . Area . (0.91) . \left(1 - e^{(-k.INT.DUR)}\right) & \rightarrow 40 \leq I < 90 mm/hr \\ a_1 . ADD^{a_2} . Area . (a_5 . INT + a_6) . \left(1 - e^{(-k.INT.DUR)}\right) & \rightarrow 90 \leq I < 115\ mm/hr \\ a_1 . ADD^{a_2} . Area . (1.00) . \left(1 - e^{(-k.INT.DUR)}\right) & \rightarrow I \geq 115\ mm/hr \end{cases} \tag{6-4}$$

Road and carpark surfaces

MEDUSA also uses a first order decay relationship to represent sediment wash-off from road surfaces (equivalent to Eqn. 6-1 for roof TSS) (Egodawatta & Goonetilleke 2008). Similarly, the initial amount of available pollutant, w_0, on the road surface was found to have a power relationship to the number of antecedent dry days (as per Eqn. 6-2).

The capacity factor, C_f, for road runoff was found by Egodawatta and Goonetilleke (2008) to have a step-wise relationship with rainfall intensity, *INT*, as shown:

$$C_f = \begin{cases} a_7.INT & \rightarrow INT < 40\ mm/hr \\ 0.50 & \rightarrow 40 \leq INT < 90\ mm/hr \\ a_8.INT + a_9 & \rightarrow 90 \leq INT < 130\ mm/hr \\ 1.0 & \rightarrow INT \geq 130\ mm/hr \end{cases} \quad (6\text{-}5)$$

However, as the rainfall intensities in Christchurch are much lower than the minimum intensity threshold of 40 mm/hr, a constant of 0.25 was found to provide a reasonable fit when the model was calibrated against the untreated runoff dataset.

Substituting Eqn. 6-2 and 6-5 into Eqn. 6-1 gives the following model equation for road TSS (g):

$$TSS_{Road} = \begin{cases} Area.(a_1.ADD^{a_2}).(0.25).(1 - e^{-k.INT.DUR}) & \rightarrow INT < 20\ mm/hr \\ Area.(a_1.ADD^{a_2}).(a_7.INT).(1 - e^{-k.INT.DUR}) & \rightarrow INT < 40\ mm/hr \\ Area.(a_1.ADD^{a_2}).0.50.(1 - e^{-k.INT.DUR}) & \rightarrow 40 < INT < 90\ mm/hr \\ Area.(a_1.ADD^{a_2}).(a_8.INT + a_9).(1 - e^{-k.INT.DUR}) & \rightarrow 90 \leq INT < 130\ mm/hr \\ Area.(a_1.ADD^{a_2}).1.00.(1 - e^{-k.INT.DUR}) & \rightarrow INT \geq 130\ mm/hr \end{cases} \quad (6\text{-}6)$$

The same equation is used in the model for carpark TSS, as the primary pollutant sources (and their associated build-up and wash-off processes) are similar: vehicular sources of sediment, zinc and copper, and some atmospheric deposition.

The effects of different traffic levels and vehicle types on pollutant generation from carparks and roads are accounted for by using separate categories in MEDUSA. Roads are categorised by their hierarchy – major arterial, minor arterial, collector, local and private roads – as this accounts for traffic intensity, vehicle type (cars and/or heavy vehicles) and frequency of street sweeping, Carparks are categorised by land use – commercial or industrial – as this accounts for vehicle type and amount of vehicle manoeuvring across the carpark surface.

6.2.3 Representing heavy metals build-up and wash-off from urban surfaces

Overview

Total copper and zinc build-up on urban impermeable surfaces during the dry period between rain events as a result of: 1) atmospheric dry deposition of sediment to which the metal is adsorbed, and 2) direct deposition of particulate copper and zinc from vehicles (refer to Chapter 2, Section 2.2.4). During rain, direct dissolution of copper and zinc surfaces occurs due to the acidity of the rain, as well as some additional direct deposition of particulate metals from vehicles and industrial emissions. However, unlike sediment, the build-up and wash-off of heavy metals has been observed to be related to a wider range of rainfall parameters that the number of antecedent dry days or rainfall intensity, as described in the following sections.

Roof surface build-up and wash-off

Several studies (He *et al.* 2001; Pennington & Webster-Brown 2008; Wicke *et al.* 2014) describe how metal concentrations (both dissolved and particulate) vary during a rainfall event. A decreasing exponential decay profile is typically followed, with a first flush period of highest concentration followed by a move to steady state conditions where the concentrations approximate a constant level.

MEDUSA therefore uses a first order decay relationship from a first flush concentration of a metal '*X*' ($[X]_0$) to an asymptote under steady-state concentrations ($[X]_{est}$), to calculate the runoff metal loads from a contributing roof surface, $[X]_{Roof}$ (mg), as shown:

$$X_{Roof} = \begin{cases} [X]_0 . Area . \frac{1}{1000.k} . C_f (1 - e^{-k.INT.DUR}) & \rightarrow DUR < Z \\ [X]_{est} . Area . INT . (DUR - Z) + [X]_0 . Area . \frac{1}{1000.k} . C_f (1 - e^{-k.INT.Z}) & \rightarrow DUR \geq Z \end{cases} \quad (6\text{-}7)$$

where	$[X]_0$	First flush concentration of metal X	(mg/L)
	$[X]_{est}$	Steady state concentration of metal X	(mg/L)
	k	Wash-off coefficient	(mm^{-1})
	I	Rainfall intensity	(mm/hr)
	DUR	Duration	(hours)
	Z	Time at which steady state conditions are reached	(hours)

Wicke *et al.* (2010) studied the relationship of *first flush* total copper and zinc concentrations, $[Cu]_0$ and $[Zn]_0$, to pH, antecedent dry days and rainfall intensity, for various roof materials. Total copper was found to have power relationships to all three variables, while total zinc was found to have a linear relationship to pH and a power relationship to antecedent dry days and rainfall intensity. Accordingly, $[X]_0$ can be expressed for copper (Eqn. 6-8) and zinc (Eqn. 6-9) as:

$$[Cu]_0 = (b_1 . PH^{b_2})(b_3 . ADD^{b_4})(b_5 . INT^{b_6}) \quad (6\text{-}8)$$

$$[Zn]_0 = (b_1 . PH + b_2) . (b_3 . ADD^{b_4}) . (b_5 . INT^{b_6}) \quad (6\text{-}9)$$

where	b_1 to b_6	Coefficients	(dimensionless)
	PH	Rainfall pH	(pH standard units)
	ADD	Number of antecedent dry days	(days)
	INT	Rainfall intensity	(mm/hr)

Wicke *et al.* (2010) also studied the relationship of total copper and zinc concentrations to rainfall pH in *steady state* conditions for various roof materials. Total copper was again found to have a power relationship with pH (Eqn. 6-10), while total zinc was found to have a linear relationship (Eqn. 6-11).

$$[Cu]_{est} = b_7 . PH^{b_8} \quad (6\text{-}10)$$

$$[Zn]_{est} = c_7 . PH + c_8 \tag{6-11}$$

where b_7, b_8 Copper coefficients (dimensionless)

c_7, c_8 Zinc coefficients (dimensionless)

PH Rainfall pH (pH standard units)

The wash-off coefficient, k, from Eqn. 6-7 is a constant value, relating the rate of exponential decay in the concentration to each particular metal. At the time when the metal concentration first reaches steady state concentration (i.e. at stationary time, Z), the steady state concentration can be expressed as:

$$[X]_{est} = [X]_0 . e^{-kIZ} \tag{6-12}$$

Eqn. 6-12 can then be solved for k:

$$k = \frac{-\ln\left(\frac{[X]_{est}}{[X]_0}\right)}{INT.Z} \tag{6-13}$$

Total copper is therefore calculated in the model based on Eqn. 6-7, using the following equation sequence:

$$[Cu]_0 = (b_1 PH^{b_2}).(b_3 . ADD^{b_4}).(b_5 . INT^{b_6}) \tag{6-14}$$

$$[Cu]_{est} = b_7 . PH^{b_8} \tag{6-15}$$

$$k = \frac{-\ln\left(\frac{[Cu]_{est}}{[Cu]_0}\right)}{INT.Z} \tag{6-16}$$

$$TCu_{Roof} = \begin{cases} [Cu]_0 . Area . \frac{1}{1000.k} (1 - e^{-k.INT.DUR}) & \rightarrow DUR < Z \\ [Cu]_{est} . Area . INT . (DUR - Z) + [Cu]_0 . Area . \frac{1}{1000.k} (1 - e^{-k.INT.Z}) & \rightarrow DUR \geq Z \end{cases} \tag{6-17}$$

Similarly, total zinc is calculated in the model as follows:

$$[Zn]_0 = (b_1 . PH + b_2).(b_3 . ADD^{b_4}).(b_5 . INT^{b_6}) \tag{6-18}$$

$$[Zn]_{est} = b_7 . PH + b_8 \tag{6-19}$$

$$k = \frac{-\ln\left(\frac{[Zn]_{est}}{[Zn]_0}\right)}{INT.Z} \tag{6-20}$$

$$TZn_{Roof} = \begin{cases} [Zn]_0 . Area . \frac{1}{1000.k} . (1 - e^{-k.INT.DUR}) & \rightarrow DUR < Z \\ [Zn]_{est} . Area . INT . (DUR - Z) + [Zn]_0 . Area . \frac{1}{1000.k} (1 - e^{-k.INT.Z}) & \rightarrow DUR \geq Z \end{cases} \tag{6-21}$$

Road and carpark build-up and wash-off

Based on several studies (Hallberg *et al.* 2007; Davis & Birch 2010), the heavy metal load (mg) in road runoff (including copper and zinc) is assumed to approximate a portion of the TSS load, as follows:

$$TCu_{Road} = \frac{1}{1000} g_1 . TSS_{Road} \tag{6-22}$$

$$TZn_{Road} = \frac{1}{1000} h_1 . TSS_{Road} \tag{6-23}$$

where g_1, h_1 Proportionality coefficients (dimensionless)

As the heavy metal sources in carparks are similar to road surfaces, the same relationship is also assumed for carpark runoff total heavy metal loads (mg), as follows:

$$TCu_{Carpark} = \frac{1}{1000} i_1 . TSS_{Carpark} \tag{6-24}$$

$$TZn_{Carpark} = \frac{1}{1000} j_1 . TSS_{Carpark} \tag{6-25}$$

where i_1, j_1 Proportionality coefficients (dimensionless)

All surfaces dissolved metals loads

While the percent of heavy metals in dissolved form can vary in response to factors such as TSS concentration or the presence of alkalinity (Sansalone & Buchberger 1997b), the model assumes that the ratio of dissolved to particulate metals is relatively constant for any given surface type, as the heavy metal build-up and wash-off processes remain the same for that surface across multiple rain events. Accordingly, dissolved metals loads (mg) for all roof, road and carpark surfaces are calculated as a proportion of the total metal load in the model, as follows:

$$DissCu_{Surface} = l_1 . TCu_{Surface} \tag{6-26}$$

$$DissZn_{Surface} = m_1 . TZn_{Surface} \tag{6-27}$$

where l_1, m_1 Proportionality coefficients (dimensionless)

6.2.4 Derivation of model coefficient values from literature

As outlined in Sections 6.2.2 and 6.2.3, there are several coefficients used within the model to describe how each pollutant relates to rainfall characteristics. Prior to collecting untreated runoff samples for this PhD research, an initial value for each coefficient was derived either from international peer-reviewed literature or previous Christchurch-specific field data where available.

TSS: Build-up coefficients

Egodawatta *et al.* (2007) and Egodawatta *et al.* (2009) studied particle build-up on road and roof surfaces, respectively, and found that the behaviour could be represented by a power relationship as shown in Eqn. 2. A method of least squares was used to create a line of fit to the field data for build-up on surfaces (g/m^2) against the number of antecedent dry days. The coefficient values obtained from the equation of the line of fit were 0.43 and 0.226 for a_1 and a_2, respectively, for roof surfaces and 1.65 and 0.16 respectively for road surfaces. These same values have been used in MEDUSA, with the values for carpark surfaces assumed to be the same as for roads.

TSS: Capacity factor coefficient, Cf

Capacity factor, C_f, is related to the capacity of rainfall to entrain and wash-off accumulated pollutants. C_f has been found to depend on rainfall intensity, INT (i.e. it increases with rainfall intensity in a step-wise manner) (Egodawatta & Goonetilleke 2008; Egodawatta *et al.* 2009). However, the relationship of C_f to intensity was found to differ between roof and road surfaces. Predicted and observed values from Egodawatta and Goonetilleke (2008) and Egodawatta *et al.* (2009) were compared to derive estimated values of C_f to intensity, as shown in Figure 6-2 and Figure 6-3, for roof and road surfaces, respectively.

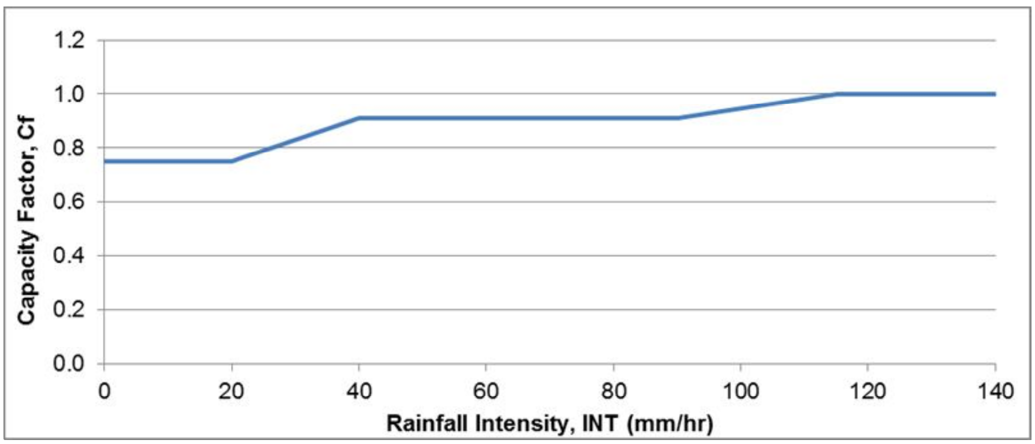


Figure 6-2: Capacity Factor relationship to rainfall intensity for roof surfaces (Data source: Egodawatta *et al.* (2009))

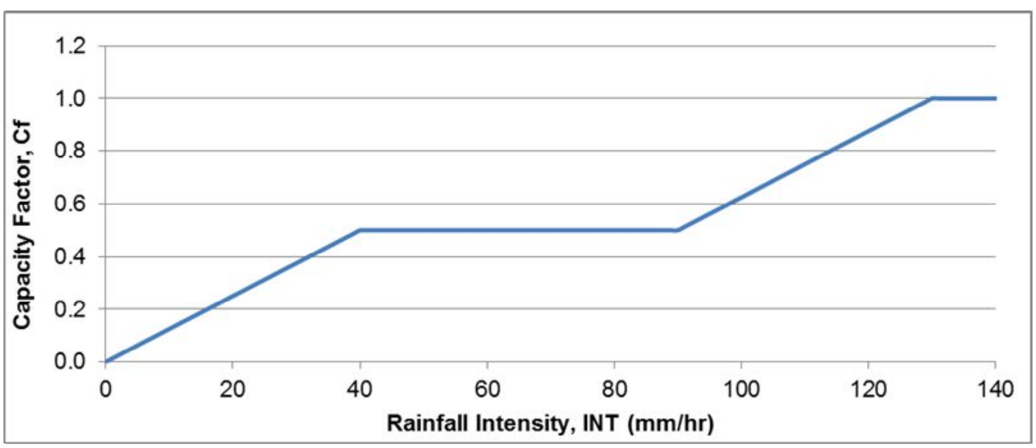


Figure 6-3: Capacity Factor relationship to rainfall intensity for road surfaces (Data source: Egodawatta and Goonetilleke (2008))

The equations of the step-wise function that describes the line of best fits shown in Figure 6-2 and Figure 6-3 give the values of the coefficients to be used in the model, as summarised in Table 6-1.

Table 6-1: Capacity Factor and coefficient values for varying rainfall intensities (Eqns. 6-3 and 6-5)

Rainfall intensity bands (mm/hr)	Roof Surfaces				Road Surfaces			
	Form of C_f equation	a_1	a_2	Constant	Form of C_f equation	a_1	a_2	Constant
$INT < 20$	Constant	--	--	0.75	Constant	--	--	0.25
$20 \leq INT < 40$	$a_3.INT + a_4$	0.008	0.59	--	$a_7.INT$	0.0125	--	
$40 \leq INT < 90$	Constant	--	--	0.91	Constant	--	--	0.5
$90 \leq INT < 115$	$a_5.INT + a_6$	0.0036	0.59	--	$a_8INT + a_9$	0.0125	-0.625	--
$115 \leq INT < 130$	Constant	--	--	1.00	$a_8INT + a_9$	0.0125	-0.625	--
$INT \geq 130$	Constant	--	--	1.00	Constant	--	--	1.00

As similar build-up and wash-off processes occur in carparks as for road surfaces, the same coefficient values (and equations) were used as the default literature-derived values for carpark surfaces.

TSS: Wash-off coefficient, k

The wash-off coefficient, k, was identified by analysis of field data by Egodawatta *et al.* (2009) to have an optimum value of 9.33×10^{-3} for roof surfaces and 8.0×10^{-4} for road surfaces. k primarily varies with surface type and texture.

Roof heavy metals: pH

Wicke et. al (2010, unpublished) measured stationary copper and zinc concentrations, Cu_{est} and Zn_{est}, against pH in runoff from both new and old roof material, using a rainfall simulator (Table 6-2). This data was plotted and a line of fit drawn from these data points (Figure 6-4), which identified whether the concentration-pH relationship was a power or linear relationship. The equations of the lines of fit provide the values of the coefficients to be used in the MEDUSA model (Table 6-3).

Table 6-2: Measured stationary copper and zinc concentration at varying pH for different roof materials

Roof Material	$[X]_{est}$ (mg/L)		
	pH = 4.2	pH = 6.3	pH = 7.72
Copper (new)	1.040	0.164	0.126
Copper (2 years old)	1.458	0.221	0.165
Galvanised steel (new)	1.193	0.646	0.407
Galvanised steel (old)	2.227	1.198	0.617

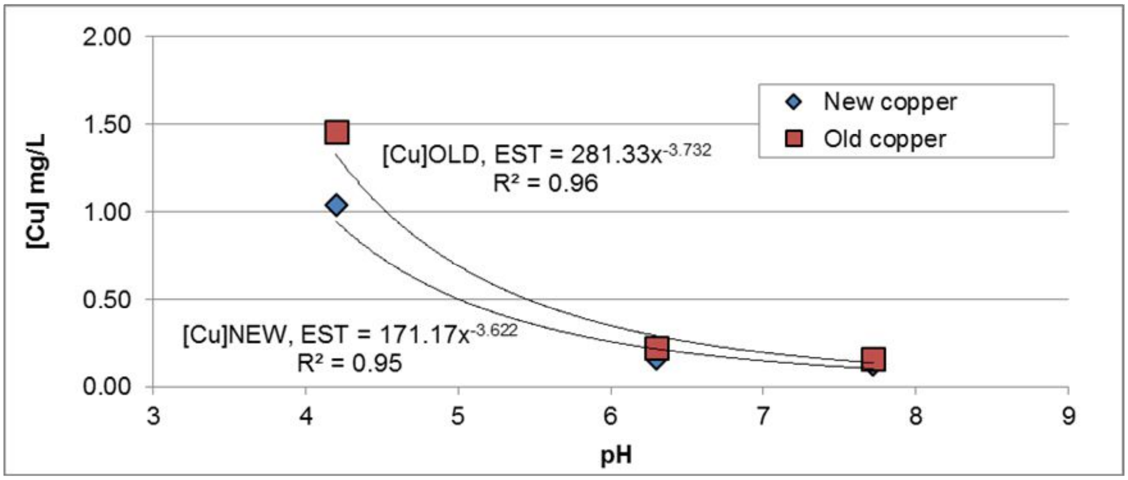


Figure 6-4: Relationships of stationary copper concentrations to pH for new and old roofs

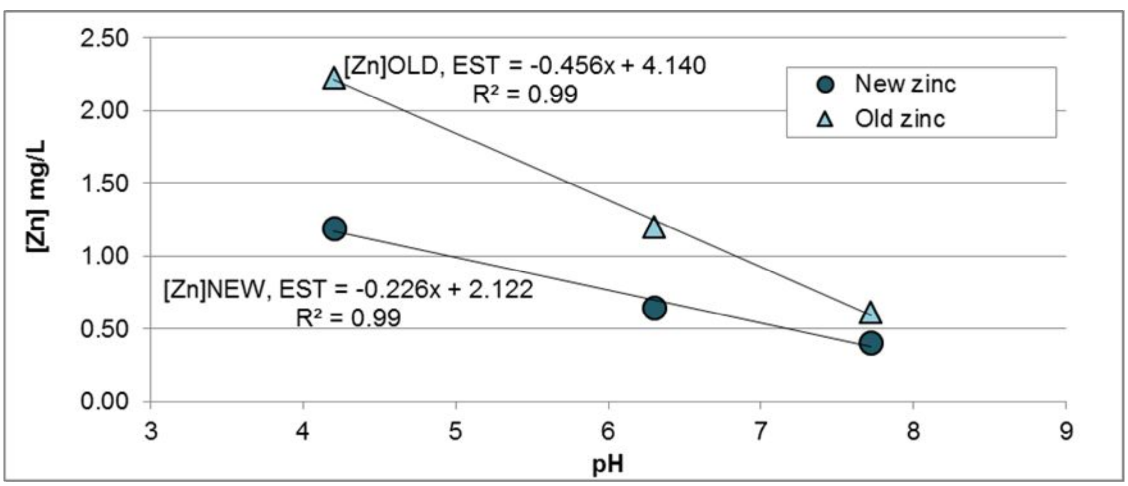


Figure 6-5: Relationships of stationary zinc concentrations to pH for new and old roofs

The equations of the line of fits shown in Figure 6-4 and Figure 6-5 give the default values of the coefficients that are used in the model, as summarised in Table 6-3. These default values assume copper loads are only generated from copper roofs and zinc loads are only generated from zinc-based roofs (e.g. galvanised steel, Zincalume ®).

Table 6-3: Equations and default coefficient values used in MEDUSA for steady state copper and zinc concentrations (Eqns. 6-10 and 6-11)

Roof material	Relationship	Metal	$[X]_{est}$ (mg/L)
New copper roof	Power	Copper	$171.17\ PH^{-3.622}$
Old copper roof	Power	Copper	$281.33\ PH^{-3.732}$
New galvanised roof	Linear	Zinc	-0.226 PH + 2.122
Old galvanised roof	Linear	Zinc	-0.456 PH + 4.140
Assumed relationship where no experimental data available:			
New Zincalume® roof	Linear	Zinc	-0.226 PH + 2.122
Old Zincalume® roof	Linear	Zinc	-0.456 PH + 4.140

From the same set of experiments, Wicke et al (2010, unpublished) measured initial copper and zinc concentrations, Cu_{init} and Zn_{init}, against varying pH, as shown in Table 6-4. Unlike steady state conditions where old material produced a higher steady state concentration than new material, the initial concentrations of metals were higher in new material than in old material. Lines of fit drawn from these data points (Figure 6-6 for copper and Figure 6-7 for zinc) identified whether the concentration-pH relationship was a power or linear relationship.

Table 6-4: Measured initial copper and zinc concentrations at varying pH for different roof materials

Roof Material	$[X]_{init}$ (mg/L)		
	pH = 4.2	**pH = 6.3**	**pH = 7.72**
Copper (new)	1.715	0.402	0.232
Copper (2 years old)	1.164	0.176	0.255
Galvanised steel (new)	2.633	2.196	1.191
Galvanised steel (old)	1.608	1.290	0.666

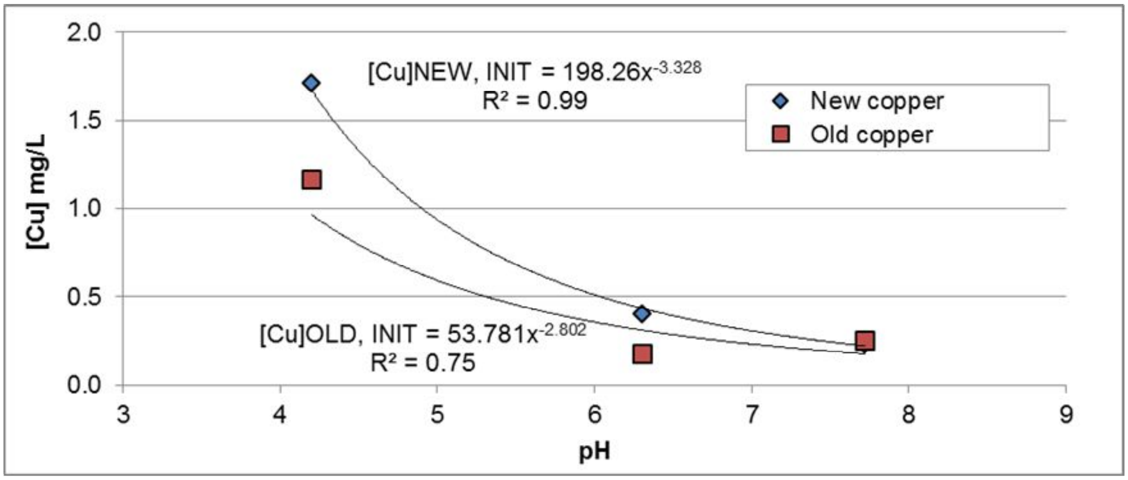


Figure 6-6: Relationships of initial copper concentrations to pH for new and old roofs

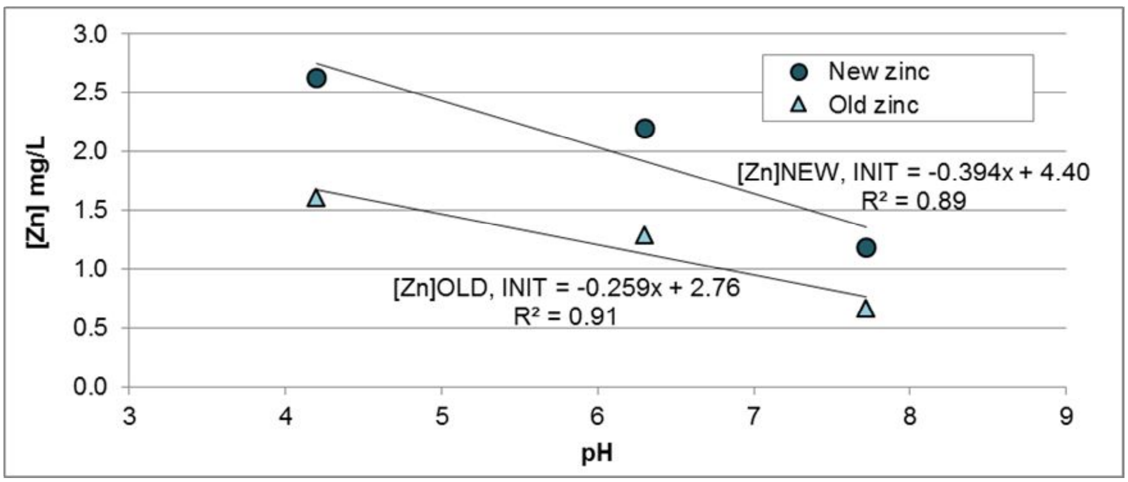


Figure 6-7: Relationships of initial zinc concentrations to pH for new and old roofs

The equations of the line of fits shown in Figure 6-6 and Figure 6-7 provided the values of the coefficients to be used in the model, as summarised in Table 6-5.

Table 6-5: Equations and default coefficient values used in MEDUSA for initial copper concentrations (Eqns. 6-8 and 6-9)

Roof material	Relationship	Metal	$[X]_{est}$ (mg/L)
New copper roof	Power	Copper	$198.26\ PH^{-3.328}$
Old copper roof	Power	Copper	$53.781\ PH^{-2.802}$
New galvanised roof	Linear	Zinc	-0.394 PH + 4.40
Old galvanised roof	Linear	Zinc	-0.259 PH + 2.76
Assumed relationship where no experimental data available:			
New Zincalume® roof	Linear	Zinc	-0.394 PH + 4.40
Old Zincalume® roof	Linear	Zinc	-0.259 PH + 2.76

Roof heavy metals: Antecedent dry days

The relationship between first flush and steady state pollutant concentrations (i.e. $[X]_0$ to $[X]_{est}$) as a function of the number of antecedent dry days was taken from experiments undertaken by He *et al.* (2001) (Table 6-6). In that study, a rainfall simulator was used to simulate rain events (at pH = 4.3, intensity = 4-8 mm/h, duration = 120 minutes) after various lengths of antecedent dry periods on new and old copper roofing and new zinc roofing.

Table 6-6: Ratio of first flush to steady state copper and zinc concentrations in relation to number of antecedent dry days

Roof Material	Ratio of $[X]_0$ to $[X]_{est}$		
	ADD = 1 day	**ADD = 7 days**	**ADD = 90 days**
Copper (new material)	1.24	1.31	1.87
Copper (old material) [1]	1.22	2.56	3.34
Zinc (new material)	0.97	1.15	1.24

[1] 'Old material' data taken from a 41-year-old copper roof panel

The equations of the line of fits of this data (Figure 6-8 and Figure 6-9) gave the values of the coefficients to be used in the MEDUSA model, as summarised in Table 6-7.

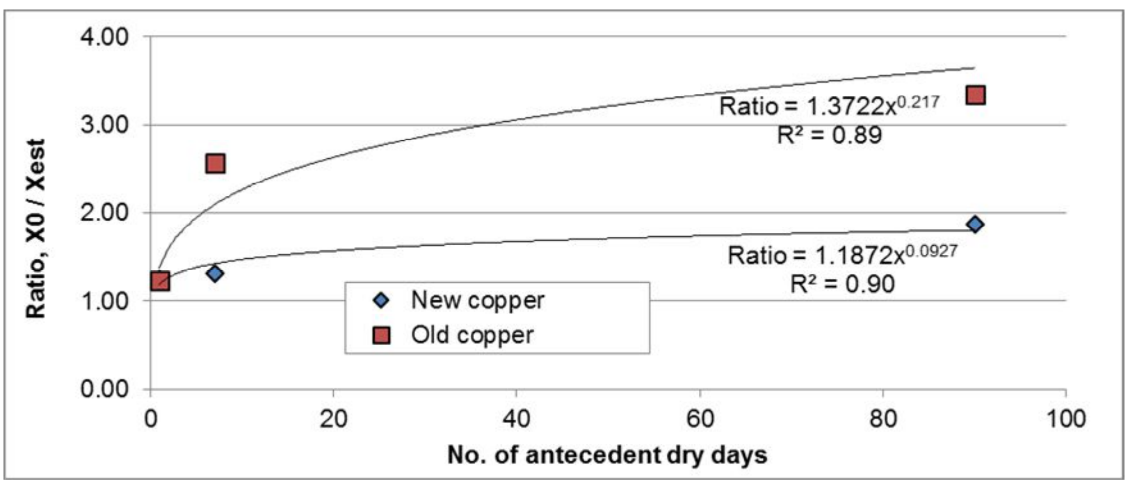


Figure 6-8: Ratio of first flush to stationary copper concentrations against number of antecedent dry days

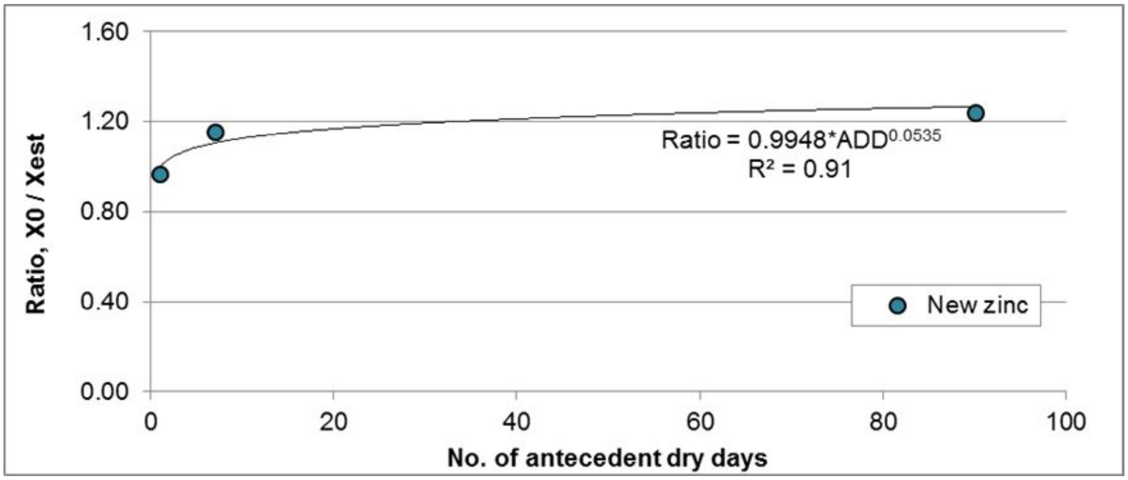


Figure 6-9: Ratio of first flush to stationary zinc concentrations against number of antecedent dry days

Table 6-7: Equations and default coefficient values used in MEDUSA for relating initial metal concentrations to ADD (Eqns. 6-8 and 6-9)

Roof material	Relationship	Metal	Multiplier
New copper roof	Power	Copper	$1.1872 \cdot ADD^{0.0927}$
Old copper roof	Power	Copper	$1.3722 \cdot ADD^{0.217}$
New galvanised roof	Power	Zinc	$0.9948 \cdot ADD^{0.0535}$
Assumed relationship where no experimental data available:			
Old galvanised roof [1]	Power	Zinc	$0.9948 \cdot ADD^{0.0535}$
New Zincalume® roof [1]	Power	Zinc	$0.9948 \cdot ADD^{0.0535}$
Old Zincalume® roof [1]	Power	Zinc	$0.9948 \cdot ADD^{0.0535}$

[1] Assumed to be same as for new galvanised roof

Roof heavy metals: Rainfall intensity

He et al. (2001) also studied the effects of rainfall intensity on metal concentrations from roof runoff and found the ratio of first flush to steady state metal concentration decreased as rainfall intensity increased (Table 6-8). A rainfall simulator was used, with pH set to 4.3 and rainfall durations of 8, 2 and 1 hour(s) for ~1 mm/hr, 8 mm/hr and 20 mm/hr conditions, respectively.

Table 6-8: Measured initial copper and zinc concentrations at varying rainfall intensities for different roof materials

Roof Material	Ratio of $[X]_0$ to $[X]_{est}$		
	INT ~1 mm/hr	INT = 8 mm/hr	INT = 20 mm/hr
Copper (new material) [1]	2.625	1.417	1.333
Copper (old material) [2]	3.650	2.744	2.868

[1] New material taken from a 1-year-old copper roof panel (as no constant region was reached for the <1-year-old panel)

[2] 'Old material' data taken from a 41-year-old copper roof panel

The equations of the line of fits of this data (Figure 6-10) gave the values of the coefficients to be used in the MEDUSA model, as summarised in Table 6-9. There was insufficient data to provide an estimate of the ratio for zinc concentrations from a zinc roof. It is therefore assumed in the default values for MEDUSA that new and old zinc roofs (i.e. galvanised and Zincalume®) follow the same expression as for new and old copper roofs, respectively, as the influence of rainfall intensity on the dissolution and wash-off of zinc from a zinc-based roof metal is expected to be similar to that of copper release from a copper roof.

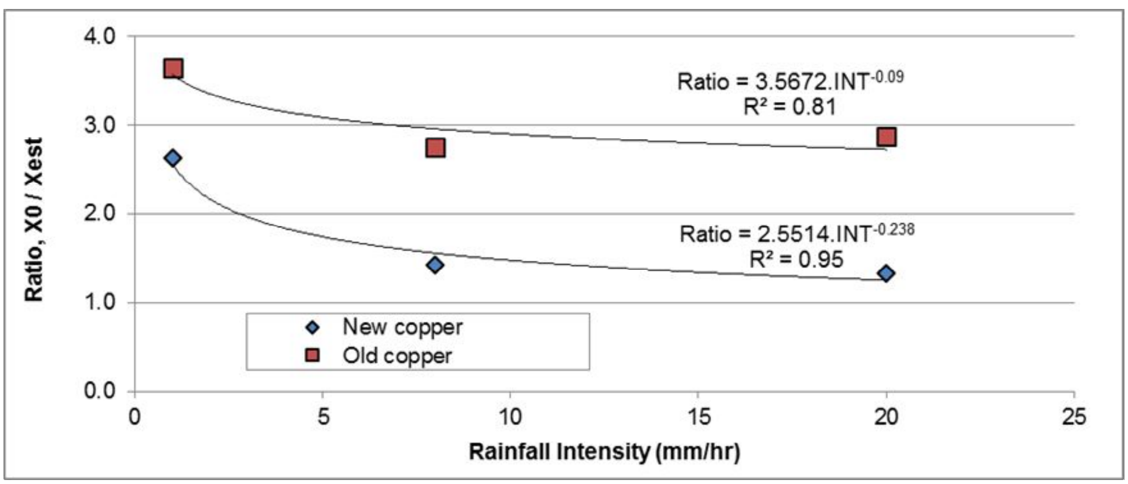


Figure 6-10: Ratio of first flush to stationary copper concentrations against rainfall intensity

Table 6-9: Equations and default coefficient values used in MEDUSA for relating initial metal concentrations to rainfall intensity (Eqns. 6-8 and 6-9)

Roof material	Relationship	Metal	Multiplier
New copper roof	Power	Copper	$3.57 \ast \text{Intensity}^{-0.09}$
Old copper roof	Power	Copper	$2.55 \ast \text{Intensity}^{-0.238}$
Assumed relationship where no experimental data available:			
New galvanised roof [1]	Power	Zinc	$3.57 \ast \text{Intensity}^{-0.09}$
Old galvanised roof [2]	Power	Zinc	$2.55 \ast \text{Intensity}^{-0.238}$
New Zincalume® roof [1]	Power	Zinc	$3.57 \ast \text{Intensity}^{-0.09}$
Old Zincalume® roof [1]	Power	Zinc	$2.55 \ast \text{Intensity}^{-0.238}$

[1] Assumed to be same as for new copper roof
[2] Assumed to be same as for old copper roof

Roof heavy metals: Stationary time, Z

While the time to reach steady state conditions, Z, is difficult to estimate, experimental results of copper concentration against rain volume from He *et al.* (2001) show steady conditions can be approximated to have been reached at 5 L/m^2. At an assumed average rainfall intensity of 5 mm/hr (i.e. a typical intensity that could be expected in most climate zones), this volume per m^2 would be reached after 60 minutes (i.e. Z = 1 hr) and therefore this is the default value of Z used in the heavy metal model equations. For the purposes of the model, the time to reach steady state conditions is assumed to be constant.

Road and carpark heavy metals: Proportionality coefficients relating metals to TSS

The value of the coefficients used to express the concentration relationships of metals to TSS in road and carpark runoff were taken from Table 6-3 of CCC's Waterways Wetlands and Drainage Guide (Christchurch City Council 2003). The table provides recommended provisional mean concentrations of pollutants for Christchurch, and these values are used to provide ratios of heavy metals to suspended solids, as shown in Table 6-10. The same values have been used for both road and carpark surfaces.

Table 6-10: Coefficients of heavy metals proportionality to TSS (Eqns. 6-22 to 6-25)

Pollutant	Flow weighted mean concentration factor	Ratio to suspended solids concentration
TSS (mg/m^3)	33,000 [1]	1.0
Copper (µg/m^3)	50	1.5
Zinc (µg/m^3)	400	12.1

[1] Value for catchment of less than 10 ha

All surfaces heavy metals: Proportionality coefficients relating dissolved metals to total metals

Wicke *et al.* (2014) analysed the proportion of total copper and total zinc measured in dissolved form in runoff from copper- and zinc-based roof materials. The average value of the percent in dissolved form from this study was used as the default coefficient values for roof surfaces in MEDUSA (i.e. the coefficient is empirically-based; Table 6-11). Likewise, the coefficients used to express the proportion of metals in dissolved form based on total metal concentrations were taken from percent dissolved values reported by Helmreich *et al.* (2010) and Zuo *et al.* (2012) in their studies of urban road runoff. As no data could be found for dissolved fractions of heavy metals in carpark runoff, the model assumed the same proportionality as road runoff.

Table 6-11: Coefficients of dissolved metals proportionality to total metals (Eqns. 6-26 to 6-27)

Pollutant	Surface Type			
	New roof	Old roof	Road	Carpark
Copper[1]	0.78	0.78	0.30	0.30
Zinc[2]	0.92	0.99	0.28	0.28

[1] Only roof surface type assumed to contribute elevated copper is copper roofs

[2] Only roof surface types assumed to contribute elevated zinc are zinc-based roof types (e.g. galvanised or Zincalume®)

Summary of default coefficient values

Table 6-12 and Table 6-13 provide a summary of the default coefficient values used in MEDUSA for roof and road/carpark surfaces, respectively.

Table 6-12: Summary of default roof coefficient values used in MEDUSA

Coefficient	Description	All roofs	New roofs	Old roofs
TSS	*(Eqn. 6-4)*			
a_1	Build-up coefficient	0.430		
a_2	Build-up coefficient	0.266		
a_3	Capacity factor coefficient for wash-off	0.008		
a_4	Capacity factor coefficient for wash-off	0.59		
a_5	Capacity factor coefficient for wash-off	0.0036		
a_6	Capacity factor coefficient for wash-off	0.59		
k	Wash-off coefficient	9.33×10^{-3}		
Total Copper	***(Eqns. 6-14 to 6-17)***		*(Copper roof only)*	
b_1	Initial Cu concentration pH coefficient		53.65	197.43
b_2	Initial Cu concentration pH coefficient		-2.800	-3.325
b_3	Initial Cu concentration ADD coefficient		1.3722	1.3722
b_4	Initial Cu concentration ADD coefficient		0.217	0.217
b_5	Initial Cu concentration intensity coefficient		2.5514	3.5672
b_6	Initial Cu concentration intensity coefficient		-0.238	-0.09
b_7	Stationary Cu concentration pH coefficient		170.33	281.33
b_8	Stationary Cu concentration pH coefficient		-3.619	-3.732
Total Zinc	*(Eqns. 6-18 to 6-21)*		*(Zinc-based roof only)*	
c_1	Initial Zn concentration pH coefficient		-0.39	-0.26
c_2	Initial Zn concentration pH coefficient		4.40	2.76
c_3	Initial Zn concentration ADD coefficient		0.9948	0.9948
c_4	Initial Zn concentration ADD coefficient		0.0535	0.0535
c_5	Initial Zn concentration intensity coefficient		2.5514	3.5672
c_6	Initial Zn concentration intensity coefficient		-0.238	-0.09
c_7	Stationary Zn concentration pH coefficient		-0.266	-0.460
c_8	Stationary Zn concentration pH coefficient		2.12	4.14
Dissolved Copper (Eqn. 6-26)			***(Copper roof only)***	
l_1	Proportionality coefficient of DissCu to TCu		0.78	0.78
Dissolved Zinc (Eqn. 6-27)			***(Zinc-based roof only)***	
m_1	Proportionality coefficient of DissZn to TZn		0.92	0.99
Shared across metals (Eqns. 6-16 to 6-17, 6-20 to 6-21)				
Z	Transition time from initial to stationary state	1.00		

Table 6-13: Summary of default road/carpark coefficient values used in MEDUSA

Coefficient	Description	All roads/carparks
TSS	*(Eqn. 6-6)*	
a_1	Build-up coefficient	0.430
a_2	Build-up coefficient	0.266
a_7	Capacity factor coefficient for wash-off	0.0125
a_8	Capacity factor coefficient for wash-off	0.0125
a_9	Capacity factor coefficient for wash-off	-0.625
k	Wash-off coefficient	8.0×10^{-4}
Total Copper (Eqns. 6-22 and 6-24)		
g_1/i_1	Proportionality coefficient of TCu to TSS	1.5
Total Zinc	*(Eqns. 6-23 and 6-25)*	
h_1/j_1	Proportionality coefficient of TZn to TSS	12.1
Dissolved Copper (Eqn. 6-26)		
l_1	Proportionality coefficient of DissCu to TCu	0.30
Dissolved Zinc (Eqn. 6-27)		
m_1	Proportionality coefficient of DissZn to TZn	0.28

6.3 Calibration of MEDUSA model to Okeover catchment

6.3.1 Initial research study site: Okeover stream water quality

MEDUSA was initially applied to the Okeover catchment in Western Christchurch (Figure 6-11). The Okeover Stream is a first-order tributary of the Avon River (O'Sullivan & Taffs 2007), with its headwaters by Waimairi Road, Ilam, and its confluence with the Avon to the east of Clyde Road (near its intersection with Kotare Street/Creyke Road). The upper catchment is typically emphemeral with water provided only from stormwater contributions from an established residential area, while the lower part of the catchment runs through the University of Canterbury grounds and is perennial with additional contributions from air-conditioning discharge and unquantified springs (O'Sullivan *et al.* 2012).

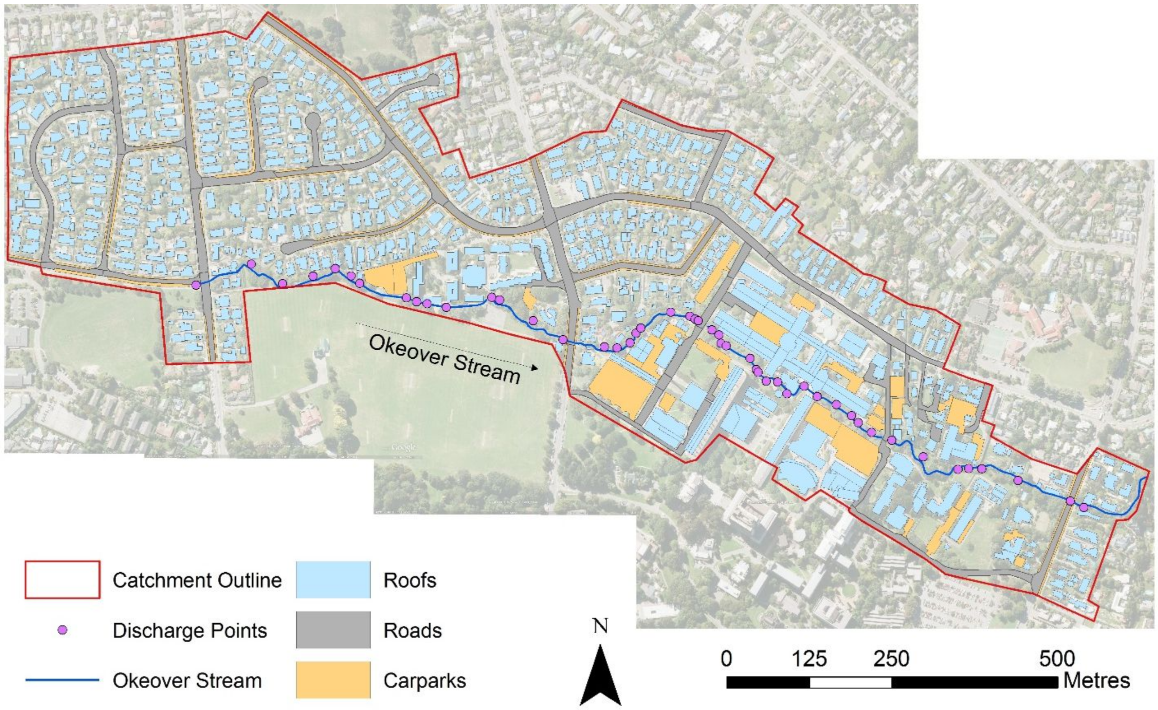


Figure 6-11: Map of Okeover catchment and its roof, road and carpark surfaces

Historically, the stream was spring-fed and maintained a perennial baseflow (Winterbourn *et al.* 2007); however, urban development of the upper catchment, with its associated increase in impervious land cover, has resulted in the majority of the springs drying up. Now, the primary baseflow contribution for the Stream comes from the seasonal discharge of air-conditioning water from University of Canterbury buildings (Winterbourn *et al.* 2007), with significant storm flows when it rains. Christchurch City Council and the University have jointly undertaken 'restoration' works on the section of the stream that passes through the University since 1996 (O'Sullivan & Taffs 2007), including riparian planting, channel shaping, construction of sediment traps, macrophyte management (Winterbourn *et al.* 2007).

Research at the University of Canterbury has identified the key sources of pollutants to the Okeover Stream as copper from air-conditioning discharges (O'Sullivan *et al.* 2012), zinc from roads and roof runoff and lead from roads and atmospheric deposition (O'Sullivan & Taffs 2007). Nickel, Cadmium, BTEX (benzene, toluene, ethylbenzene, and xylenes) and PAHs (poly-aromatic hydrocarbons) were found to be either below detection levels or at levels low enough not to be of concern (O'Sullivan & Taffs 2007).

6.3.2 Derivation of pollutant loads from sampled Okeover data

The dataset of untreated runoff sampled from a concrete tile, copper and galvanised roof and asphalt road (refer to Chapter 4) was used to calculate total event pollutant loads (L; g/event or mg/event) for each sampled surface. The event loads were calculated on a per area basis (mg/m^2 or µg/m^2) using the measured pollutant concentrations and rainfall depth accumulated over the time interval between samples, as follows:

$$L = \int_0^1 C(t) \times d(t).dt \qquad (6\text{-}28)$$

where $C(t)$ is the pollutant concentration (mg/L or µg/L) at each sampling time and $d(t)$ is the amount of rainfall (mm) that has fallen over the interval centred on each sampling time. These loads derived from the observed concentrations (hereafter, the observed loads) were then compared against model predicted pollutant loads to assess model predictive performance.

6.3.3 Calibration of model coefficient values

MEDUSA was run using the rainfall characteristics recorded for the 25 rain events sampled in the Okeover catchment (refer to Chapter 3: Section 3.7). The predicted pollutant loads were then compared against the observed loads to calibrate MEDUSA to local rainfall conditions. Optimal calibration was determined by adjusting the model coefficient values to obtain the highest Nash Sutcliffe Efficiency (NSE) value, while achieving low percent bias (PBIAS) values (refer to Section 6.3.4). No outliers were removed from the dataset as event loads were from observed data and therefore such variance and seemingly unusual event loads should be accounted for in the model.

For the total copper and total zinc model, the time to reach steady state conditions, Z, was derived from the time-series sampling from the concrete tile, copper and galvanised roof surfaces (refer to Chapter 4: Section 4.3.4).

6.3.4 Assessing model fit

The Nash-Sutcliffe model efficiency (NSE) and percent bias (PBIAS) statistics were used to assess the predictive power of the calibrated model and goodness of fit. The NSE was developed for assessing hydrological models (Nash & Sutcliffe 1970), but has also been employed for modelling sediment and nutrient loadings (Moriasi *et al.* 2007). It describes the predictive accuracy of the model in comparison to the observed data. The NSE is defined as:

$$E = 1 - \frac{\sum_{j=1}^{J}\left(x_o^j - x_m^j\right)^2}{\sum_{j-1}^{J}\left(x_n^j - \overline{x_o}\right)^2} \qquad (6\text{-}29)$$

where $\overline{x_o}$ is the mean of the observed pollutant loads, x_m^j is the modelled load and x_o^j is the observed load for rain event *j*. An efficiency, E, of 1 indicates a perfect fit between the modelled and observed loads, an efficiency of 0<E<1 indicates the model is a better predictor than the observed mean, E= 0 indicates the model is only as accurate as the observed mean, while E<0 indicates the observed mean is a better predictor than the model. Modelled and observed loads were log-transformed before the NSE was applied to reduce the influence of any peak events as they increase the sensitivity of NSE to systematic over- or under-prediction (Krause *et al.* 2005). All datapoints were used in the calculation of the NSE (i.e. the outliers removed to train the model were included in the NSE calculations and graphs of observed versus predicted loads).

The percent bias (PBIAS) is a measure of the average tendency of the model predicted values to be greater or smaller than their observed values (Gupta *et al.* 1999). It has been commonly used for hydrological models and is recognised for its ability to clearly identify poor model performance (Gupta *et al.* 1999). The PBIAS is defined as:

$$PBIAS - 100 \times \left(\frac{\sum(x_m - x_o)}{\sum x_o}\right) \tag{6-30}$$

where x_m is the modelled load and x_o is the observed load. A PBIAS value of 0 indicates a perfect fit; the smaller the PBIAS value, the better the performance of the model.

6.3.5 Development of comparative linear regression model

Linear regression (LR) models for the combined build-up and wash-off of TSS and total and dissolved copper and zinc were generated for each of the four impermeable surface types from the same dataset used to calibrate MEDUSA. The aim of the LR modelling approach was to provide a catchment-specific alternative model that the performance of the Okeover-calibrated MEDUSA could be benchmarked against. It was expected that a catchment-specific LR model would achieve better model fit than a calibrated process-based model (e.g. MEDUSA) that simulates generalised build-up and wash-off behaviour. The aim was to identify whether an acceptable model fit could be also achieved with the calibrated MEDUSA model, relative to the expected high fit of a LR model using the same type of predictor variable (i.e. rainfall characteristics). LR modelling was conducted using R (Release 3.1.3) statistical software.

Rainfall characteristics were used as independent variables in the LR model (Table 6-14). Various combinations of variables were run and the optimum model was selected as the one with the lowest Akaike Information Criterion (AIC) value (Akaike 1998). The AIC value is a measure of the *relative* quality of several comparable models derived from the same dataset, and therefore can be used to identify the preferred model. Where two models had similar AIC (i.e. difference in AIC values <3, following Burnham and Anderson (2003)) but a different number of independent variables, the model with the lower number of independent variables was adopted to reduce the effects of over-parameterisation (i.e. the most parsimonious model was found with minimal compromising of goodness of fit).

Model fit was assessed using the NSE and PBIAS metrics, as was done for the Okeover-calibrated MEDUSA model (refer to Section 6.3.4).

Table 6-14: Rainfall characteristics used in linear regression modelling

Rainfall Characteristic	Data source	Significance in pollutant generation processes
Rainfall pH	Manually measured	Rainfall is naturally acidic due to raindrops' scavenging of carbon dioxide to form carbonic acid as they fall. The low pH can dissolve metallic components of a surface (Clark *et al.* 2008; Förstner & Wittmann 2012)
Rainfall Intensity (mm/hr)	Rainfall recorded at 5-min intervals from local weather station	Both average and peak intensity were characterised for each sampled event. The intensity is an indication of the kinetic energy present that allows the entrainment and transport of particles in runoff from a surface (Egodawatta *et al.* 2007).
Number of antecedent dry days (days)		Pollutants accumulate on impermeable surfaces due to atmospheric deposition, direct deposition from vehicles, and weathering of surface, during the dry periods between rain events. Studies have shown a log or arctan relationship where pollutant build-up rates are most rapid at the start of the antecedent dry period then slower over time (Wicke et al., 2014)
Event duration (hrs)		Pollutant wash-off continues throughout a rain event, however, the rate of wash-off is generally expected to reduce (exponentially) over the course of a rain event due to the decreasing amount of available material remaining on the surface (Charbeneau & Barrett 1998).
Depth of current event (mm)		Greater rainfall depths, and therefore larger rainfall volumes, will generate larger total amounts of pollutants (Chui 1997).
Depth of preceding event (mm)		Correlation to the depth of the preceding event may indicate that the amount of material being washed off is influenced by how much material was able to be washed off in the preceding rain event and how much remained on the surface to be carried over to the current event (Brodie & Egodawatta 2011; Charters *et al.* 2015).

6.3.6 Statistical analysis methods – comparison between MEDUSA and LR model results

Statistical analysis was done using IBM®'s SPSS® Statistics (Release 22.0) software. The Sign Test was used to compare whether the distribution of MEDUSA predicted loads for each sampled surface type significantly differed from what was predicted by the corresponding LR model. This non-parametric test was used as evaluation of the distribution of pairwise differences showed the data could not be assumed to be neither normally nor symmetrically distributed (and hence neither the more powerful paired t-test nor Wilcoxon signed-rank test could be performed).

6.4 Model results

6.4.1 Optimised Okeover MEDUSA Model

The MEDUSA model produced moderate to high NSEs for all pollutants, for all four surfaces (Table 6-15). Of the four sampled surfaces, the optimised MEDUSA model was most effective at predicting road runoff pollutant loads (NSEs of 0.66-0.74). The highest total copper loads (per area) were from the copper roof, however the model is only moderately effective at predicting total copper from a copper roof (NSE of 0.46). Nonetheless, the model is quite effective at predicting dissolved copper (NSE of 0.69), which accounts for the majority of the total copper. The highest total zinc loads (per area) were from the galvanised roof, and the model is effective at predicting both total and dissolved zinc from galvanised roofs (NSEs of 0.66 and 0.68, respectively). Comparisons of MEDUSA predicted pollutant loads against observed loads (Figure 6-12 to Figure 6-16) shows that MEDUSA tends to slightly over-predict copper and zinc loads from galvanised and concrete roofs.

Calibrated TSS coefficient values for the MEDUSA model showed that the copper roof was substantially more influenced by ADD than the concrete and galvanised roofs (i.e. higher ADD coefficient values; Table 6-15). For the copper model, the copper roof was substantially more influenced by rainfall pH than the other two roof surfaces, and to a lesser extent, by average rainfall intensity. For the zinc model, the galvanised roof was more influenced by rainfall pH (particularly during steady state conditions) than the other two roof surfaces. It was also more influenced by ADD and to a lesser extent average rainfall intensity.

The linear regression model also produced moderate to high NSEs for all pollutants, for all surfaces (Table 3), and was most effective at TSS and copper loads from road runoff and zinc loads from copper roofs. The model was highly effective at predicting copper loads from copper roofs (NSEs of 0.78 and 0.79 for total and dissolved copper, respectively) and moderately effective at predicting zinc loads from galvanised roofs (NSEs of 0.59 and 0.53 for total and dissolved zinc, respectively). The linear regression model tends to under-estimate copper loads from copper roofs and zinc loads from roads; it does not tend to over-estimate pollutant loads (Figure 6-13 to Figure 6-16).

Only one rainfall variable, log-transformed rainfall duration, was found to be a common factor amongst all TSS, total copper and total zinc linear regression models for all surface types. The sole exception where duration was not included as a variable in the best-fit model was the zinc model for road runoff. Log-transformed ADD was a common variable for most of the copper and zinc models, and log-transformed average intensity was a common variable for the three roof total copper models. The depth of the previous event (log-transformed) was a common variable in three of the four TSS models, suggesting carry over of particles between events (i.e. incomplete wash-off) may be occurring under local rainfall conditions. Good predictive models were found for dissolved copper and zinc using only the total metal loads as the predictor variable. This suggests that although rainfall pH and sediment availability could be expected to influence the partitioning of metals between particulate and dissolved, in the untreated runoff, at least, the metals partitioning is relatively consistent.

The galvanised roof linear regression model for total zinc incorporated the same variables as its model for total copper, however, the two other roof surfaces differed in their model form between total copper and total zinc. The copper roof was similar, incorporating log-transformed ADD and duration, however average intensity was excluded from the zinc model. The concrete roof model incorporated duration, peak intensity and depth of previous event for zinc instead of the duration, ADD and average intensity used for copper.

Table 6-15: Optimised MEDUSA model coefficient values and model goodness of fit statistics

Surface[1]	TSS Coefficients (Eqns. 4 and 6)			NSE	PBIAS
	a_1	a_2	k		
Cr	0.6	0.25	9.33×10^{-3}	0.503	0.2
Cu	2.5	0.95	9.33×10^{-3}	0.487	-3.2
Gv	0.4	0.5	9.33×10^{-3}	0.43	-4.5
Rd	2.9	0.16	8.0×10^{-4}	0.736	0.1

[1] Cr – concrete tile roof; Cu – copper roof; Gv – galvanised roof; Rd – asphalt road

Surface	TCu Coefficients (Eqns. 14 to 17, 22)										NSE	PBIAS
	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	Z	g_1		
Cr	2	-2.8	0.5	0.217	3.57	-0.09	7	-3.73	0.75		0.55	1.67
Cu	100	-2.8	1.372	0.217	3.57	-1	275	-3.3	0.75		0.68	-5.09
Gv	2	-2.8	0.5	0.217	3.57	-0.09	7	-3.73	0.75		0.58	11.47
Rd										0.441	0.69	-0.05

Surface	TZn Coefficients (Eqns. 18 to 21, 23)										NSE	PBIAS
	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	Z	h_1		
Cr	-0.1	2	0.1	0.01	1	-3.1	-0.007	0.056	0.75		0.632	-1.71
Cu	-0.1	2	0.1	0.01	0.8	-1.3	-0.007	0.056	0.75		0.679	-7.02
Gv	-0.5	4	0.2	0.09	1.5	-2	-0.23	2.122	0.75		0.657	3.97
Rd										1.96	0.731	1.14

Surface	DCu Coefficients (Eqn 26) l_1	NSE	PBIAS
Cr	0.46	0.47	9.4
Cu	0.77	0.69	-5.8
Gv	0.28	0.59	37
Rd	0.28	0.68	4.9

Surface	DZn Coefficients (Eqn. 27) m_1	NSE	PBIAS
Cr	0.67	0.69	-5.2
Cu	0.72	0.68	-10.6
Gv	0.43	0.68	1
Rd	0.43	0.69	-3.26

Table 6-16: Linear regression model coefficient values and model goodness of fit statistics

Pollutant	Surface[1]	Intercept	ln(PH)	ln(ADDd)	ln(INTavg)	ln(INTpk)	ln(Duration)	ln(DEPTHt)	ln(DEPTHp)	lnTcu	lnTZn	NSE	PBIAS
TSS	Cr	1.18		0.01	1.57		1.03		0.39			0.69	0.1
	Cu	3.02		0.79		-0.19	1.28		0.00			0.66	-0.4
	Gv	1.73			0.24		0.85		0.77			0.72	-1.0
	Rd	2.35				1.18	0.95		0.51			0.90	0.1
TCu	Cr	-0.33		0.29		1.66	0.82		0.27			0.89	0.2
	Cu	7.39		0.63	-0.38		0.46	0.90				0.89	-0.2
	Gv	0.52		0.75	-0.03		-0.76	2.08				0.85	1.2
	Rd	-1.38					-0.19		-0.06			0.91	4.8
DCu	Cr	0.00								0.77		0.88	0.2
	Cu	-0.23								1.00		0.89	-0.1
	Gv	-0.64								0.79		0.87	1.6
	Rd	-1.31								0.97		0.90	6.3
TZn	Cr	0.86				1.30	0.94		0.31			0.87	0.2
	Cu	3.61		0.82			1.38					0.88	-0.8
	Gv	5.18		0.60	-0.18		-0.90	1.92				0.82	0.6
	Rd	0.10	0.15									0.94	3.6
DZn	Cr	0.12									0.92	0.94	0.2
	Cu	0.17									0.93	0.87	-0.7
	Gv										1.00	0.80	-2.5
	Rd	-0.28									0.96	0.92	3.7

[1] Cr – concrete tile roof; Cu – copper roof; Gv – galvanised roof; Rd – asphalt road

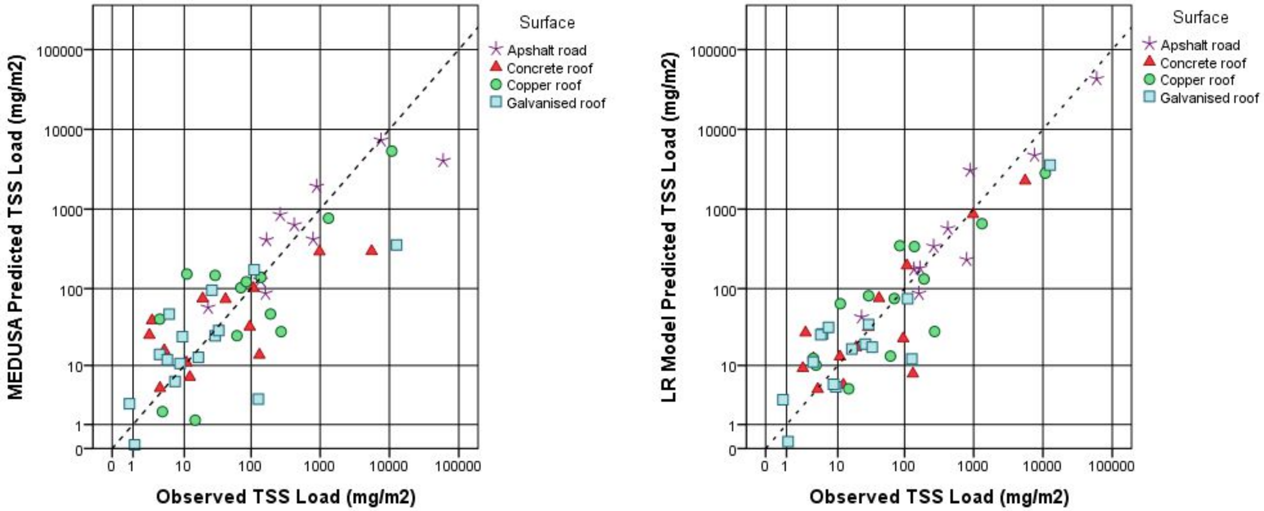


Figure 6-12: Predicted TSS loads (left: MEDUSA; right: linear regression model) against observed loads

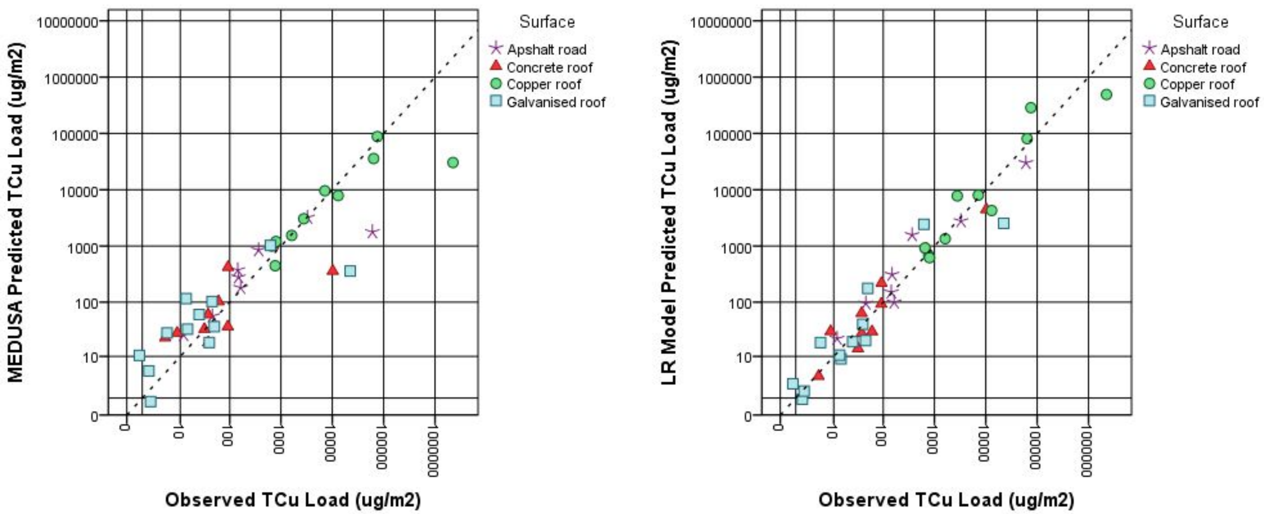


Figure 6-13: Predicted total copper loads (left: MEDUSA; right: linear regression model) against observed loads

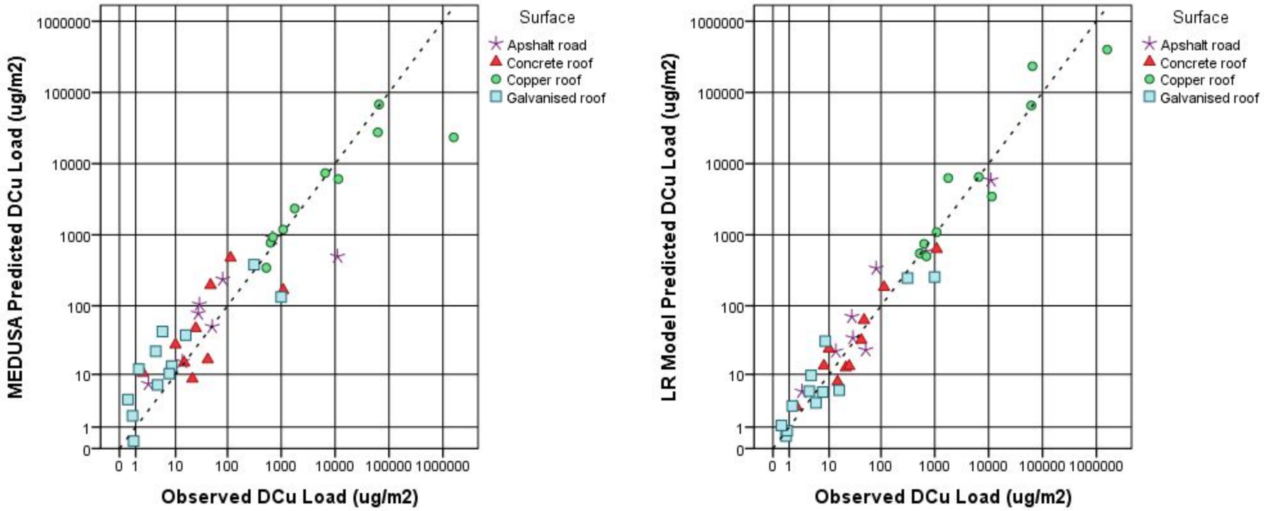


Figure 6-14: Predicted dissolved copper loads (left: MEDUSA; right: linear regression model) against observed loads

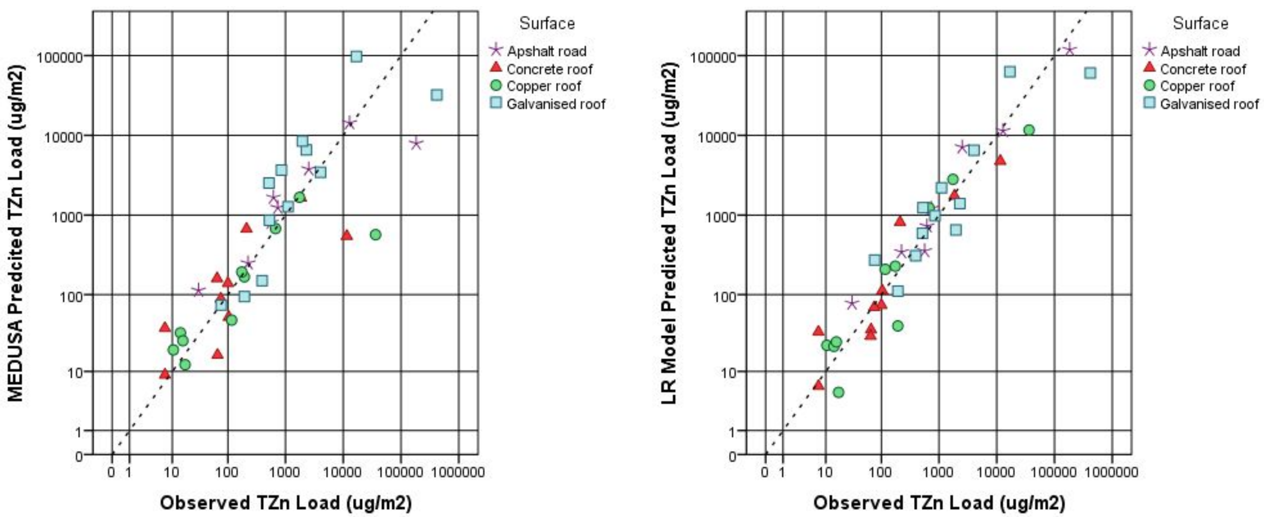


Figure 6-15: Predicted total zinc loads (left: MEDUSA; right: linear regression model) against observed loads

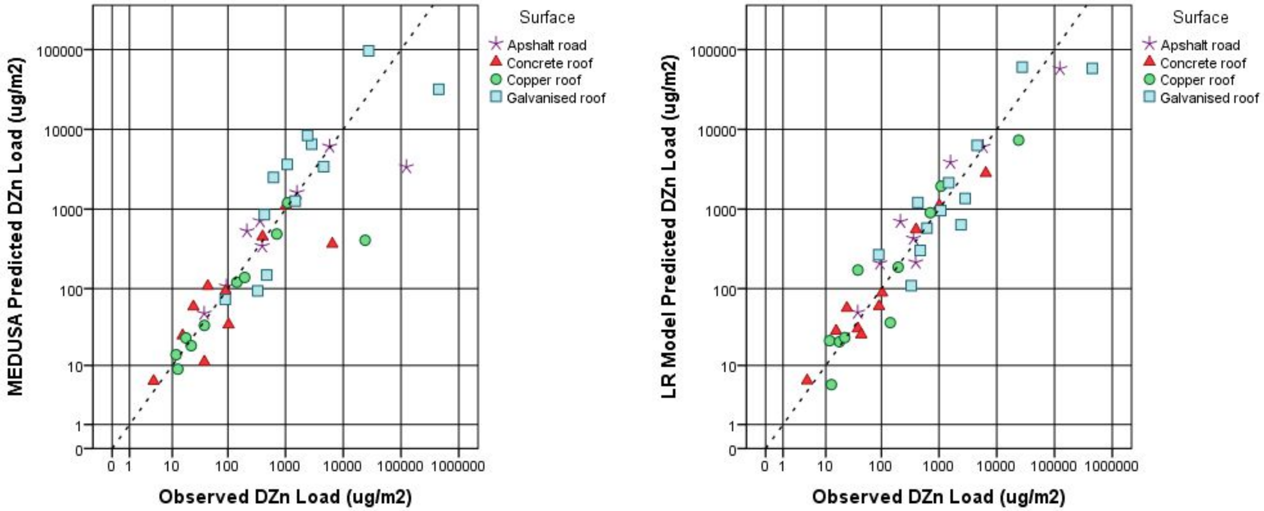


Figure 6-16: Predicted dissolved zinc loads (left: MEDUSA; right: linear regression model) against observed loads

6.4.2 Comparison of the two models

For all surfaces and pollutants, the linear regression model produced a higher NSE value than the MEDUSA model (Table 6-17). Both models were confirmed to have substantially better predictive power than using the mean load value for all surfaces and all modelled water quality parameters (i.e. all NSEs >0).

For both model approaches, the highest NSEs were seen for the road runoff water quality parameters. This is valuable because the road runoff produced high pollutant loads for sediment as well as metals. The accurate prediction of copper loads from copper roofs is also important due to the very high concentrations observed in copper roof runoff, and the LR model was substantially better than the MEDUSA model in this regard, although the MEDUSA model had a moderate NSE. Similarly, accurate prediction of galvanised roof zinc loads is also a priority, and both models produced high NSEs, although again, the LR model was a better predictor than the MEDUSA model.

Table 6-17: Comparison of NSEs and pairwise differences for the two models

Parameter	Surface	Okeover calibrated MEDUSA NSE	Linear Regression Model NSE	Sign Test		
				Median difference (TSS: mg/m^2, metals: µg/m^2)	Z	Sig.
TSS	Concrete roof	0.50	0.69	0.3	-0.8	0.42
	Copper roof	0.49	0.66	5.2	-0.4	0.69
	Galvanised roof	0.43	0.72	0.4	0.4	0.69
	Asphalt road	0.74	0.90	19.9	-2.4	**0.02 ***
TCu	Concrete roof	0.55	0.89	6.9	-1.6	0.11
	Copper roof	0.46	0.89	4,828	2.0	**0.04 ***
	Galvanised roof	0.58	0.85	7.9	-2.0	**0.04 ***
	Asphalt road	0.66	0.91	3.7	-1.2	0.23
DCu	Concrete roof	0.47	0.88	3.2	-1.6	0.11
	Copper roof	0.69	0.89	3,976	2.4	**0.02 ***
	Galvanised roof	0.59	0.87	5.1	-2.4	**0.02 ***
	Asphalt road	0.68	0.90	2.5	-2.4	**0.02 ***
TZn	Concrete roof	0.63	0.87	20.9	-2.0	**0.04 ***
	Copper roof	0.68	0.88	327	2.8	**0.00 ***
	Galvanised roof	0.66	0.82	437	-0.4	0.69
	Asphalt road	0.73	0.94	35.5	-2.4	**0.02 ***
DZn	Concrete roof	0.69	0.94	10.1	-0.9	0.42
	Copper roof	0.68	0.87	262	3.2	**0.001 ***
	Galvanised roof	0.68	0.80	433	-0.4	0.69
	Asphalt road	0.69	0.92	1.0	0.0	1.00

* Statistical significance, $p = 0.05$

The Sign Test showed that there were no statistically significant differences between the calibrated MEDUSA model and the linear regression model for roof TSS predictions, only for road TSS predictions.

However, there were statistically significant differences between the two models for the majority of surface types for copper and zinc predictions.

In the MEDUSA model, only ADD is used to predict TSS loads, regardless of surface type, based on observations by Egodawatta *et al.* (2009) of dry weather pollutant build-up on surfaces. In contrast, the optimum linear regression models for TSS differed between surface type and only the copper roof runoff model incorporated ADD. A first flush of elevated TSS has previously been observed in the copper roof runoff (Charters *et al.* 2016) and was thought to be some copper patination byproduct (developed during dry weather conditions). This may explain why ADD appears as a variable in the optimum TSS model for copper roof runoff. Gnecco *et al.* (2005) similarly did not find any correlation between runoff Event Mean Concentration (EMC) and ADD, and considered this likely to be due to the low-to-medium rainfall intensity and low total rainfall volume of their sampled events, where the amount of pollutant wash-off was too low to show differences in dry weather TSS build-up between each event. This study's rainfall is similarly of low intensity. A study within the same Okeover catchment of atmospherically-deposited TSS, copper and zinc did show that pollutant build-up was significantly influenced by ADD, however, pollutant wash-off processes had a stronger influence than build-up processes on the overall pollutant loads generated from atmospheric deposition (Murphy *et al.* 2015). The optimum TSS linear regression models for the concrete roof, galvanised roof and road surfaces all incorporated the depth of the previous rainfall event as a variable, suggesting some carryover of sediment between rain events is occurring.

All three roof surfaces incorporated the same variables into their total copper linear regression models: log-transformed ADD, average intensity and duration. The optimum galvanised roof model also incorporated total rainfall depth. In contrast, the MEDUSA model assumes rainfall pH is a significant variable relating to both initial and steady state copper concentrations, and the initial concentrations are also dependent on ADD and average intensity. The dataset used to inform the linear regression models ranged in rainfall pH from 5.1 to 7.9, which does not allow characterisation of the pollutant load's response to broader changes in pH, and may explain why no relationship to rainfall pH was seen in the linear regression models for either road or roof runoff. Therefore, for application of the model in a catchment that does not have acid rain or where copper roofs are not a concern, the linear regression model results suggest that rainfall pH is not a significant influence on metal loads in runoff.

6.5 Example application of the models to a case study catchment: Okeover Catchment, Christchurch, New Zealand

6.5.1 Overview

Both models were applied to the Okeover catchment, where the untreated runoff samples were collected, to predict the pollutant loads from individual road, roof and carpark surfaces within the catchment for a typical year of rain events. A GIS map of the Okeover catchment and its contributing impermeable surfaces was developed (Figure 6-11). Each surface type was broken down into classifications based on material, and was assigned model properties based on the closest sampled surface type from Okeover sampling data (Table 6-18). Hardstand areas such as driveways on private residential property were not included in the modelling as they were considered to proportionally contribute only a small amount of runoff into the stormwater system.

Table 6-18: Classification of Okeover impermeable surfaces using Okeover-calibrated model coefficients

Surface type	Surface classifications	Source of model coefficients
Roofs	Butynol	Okeover concrete roof
	Concrete	Okeover concrete roof
	Copper (old)	Okeover copper roof
	Decramastic (new, moderate, old)	Okeover galvanised roof
	Galvanised (new, moderate, old)	Okeover galvanised roof
	Glass	Okeover concrete roof
	Zincalume ® (new, moderate, old)	Okeover galvanised roof
Roads	Asphalt	Okeover asphalt road
Carpark	Asphalt	Okeover asphalt road

The models were run for a full year of rain events from the year 2012 (Table 6-19; refer also to Appendix G for full event details), as researchers at the University of Canterbury had measured rainfall pH for several rain events in 2012. Therefore a relatively complete set of characterised rainfall events was available, with minimal assumptions required for rainfall pH. While there will be variation from year to year, 2012 had relatively normal annual rainfall for Christchurch (Christchurch Botanic Gardens weather station recorded 631 mm annual rainfall for 2012 (NIWA 2013b); Christchurch's mean annual rainfall is 647 mm (NIWA 2013a)) and it provides an indication of the expected variation of rain events across a year. Average event loads were derived from the average of all 88 events of 2012.

Table 6-19: Rainfall event characteristics for the year 2012

Rainfall parameter	Median value (range)
Number of rain events	88
Rainfall pH	6.01 (5.19 – 7.15)
Average intensity (mm/hr)	0.53 (0.12 – 4.00)
Antecedent dry days (days)	3.0 (0.2 – 19.0)
Event duration (hours)	5.0 (1.0 – 41.0)

6.5.2 Comparison in predicted loads between MEDUSA and linear regression models

Event loads for the whole catchment were modelled for the 88 rain events of the year 2012. Boxplots of the distribution of pollutant loads show that MEDUSA and the LR models share a similar distribution for TSS, although the LR model predicts higher TSS loads than MEDUSA for roof surfaces (Figure 6-17). However, for copper and zinc road and carpark loads, the LR model distribution is markedly left skewed, with a wider range than the MEDUSA predicted loads, but lower median value (Figure 6-18). The applicability of the linear regression model is limited to the particular combination of (low intensity) rainfall characteristics of the sampled events dataset that it was developed from. The LR model is less robust in its load predictions when the model is applied to different rain events (where the rainfall characteristic values may be within the same range of those of the sampled events but the relationship between each of the characteristics for any given event is different from those of the sampled events).

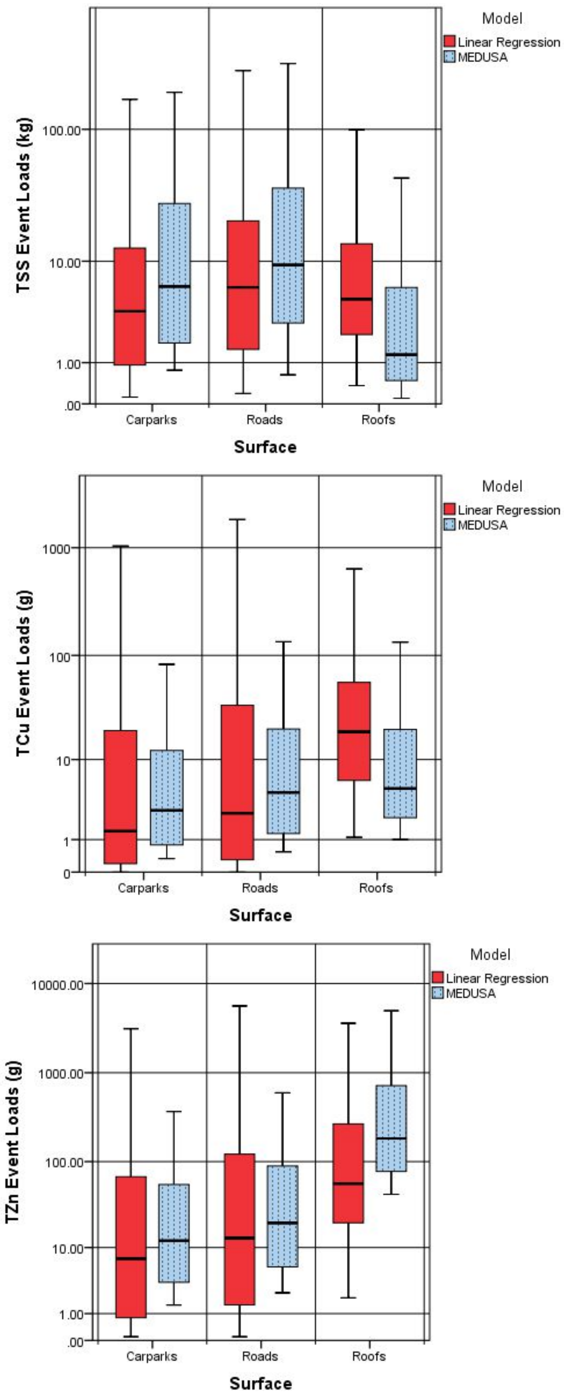


Figure 6-17: Comparative load distributions for MEDUSA and linear regression models

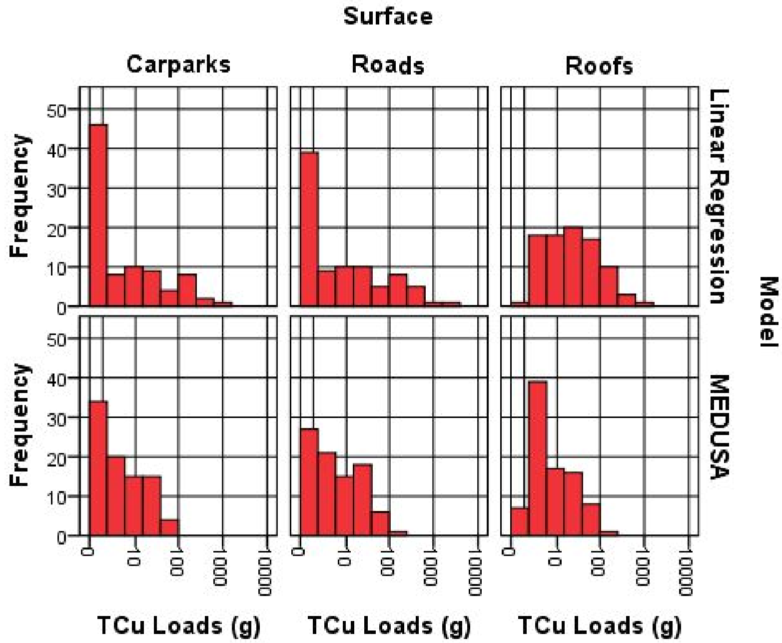


Figure 6-18: Frequency distribution of total copper loads by surface type for MEDUSA and linear regression models

6.5.3 MEDUSA-predicted average event loads

The average event loads contributed by each surface type were compared to the relative surface areas (Figure 6-19). While roof surfaces make up the majority of the modelled impermeable surfaces, they are predicted to contribute very little TSS, a disproportionally low amount of copper, but the vast majority of zinc. Conversely, road and carpark surfaces are predicted to be nearly the sole contributors of sediment and a disproportionally high amount of copper. However, further assessment of the subcategories of roof runoff show that the copper roofs at the University (within the modelled catchment) are contributing very high copper loads for their small cumulative surface area. These results yield important implications for modelling other catchments with copper roofs or cladding (as typical in architectural designs).

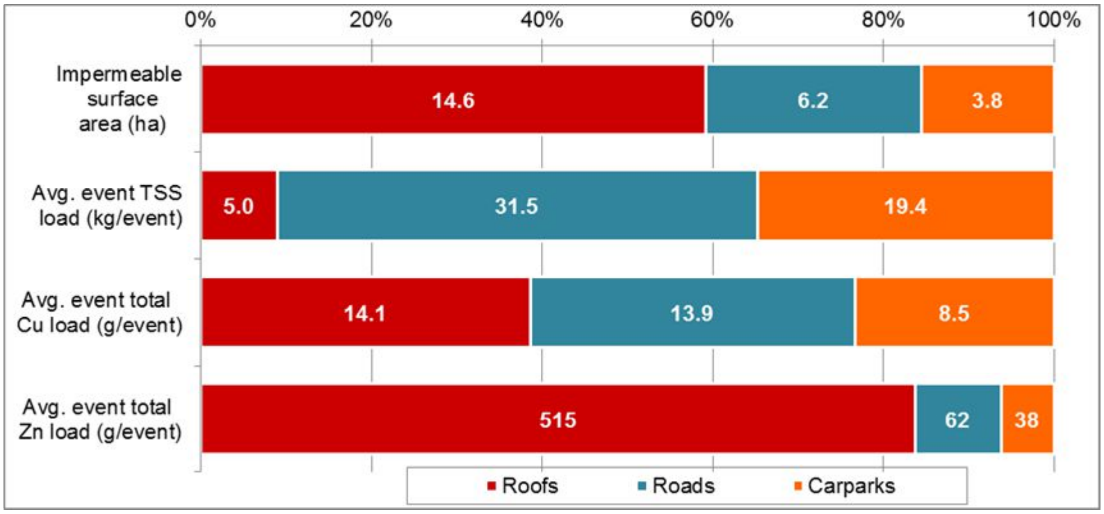


Figure 6-19: MEDUSA predicted average event loads by main surface types, compared to their relative surface area

6.5.4 Spatial distribution of loads

Average event loads were calculated for each surface based on the 88 modelled events from 2012, and mapped to show the spatial distribution of pollutant loads (Figure 6-19 to Figure 6-21). The model predicts that roads throughout the catchment are contributing the highest sediment loads, along with the two largest carparks in the University (that drain to the Okeover): the Science and Geology carparks (Figure 6-20). Total copper mapping showed that the two copper roof surfaces, despite their small area, are predicted to contribute event loads substantially higher than any other individual surface in the catchment. Of the remaining surface types, the large Science carpark is highlighted as a significant contributor of copper, along with the linear road surfaces. Zinc loads have a distinctly different spatial pattern than sediment and copper as the rate of zinc generation is much higher from any zinc-based roof material.

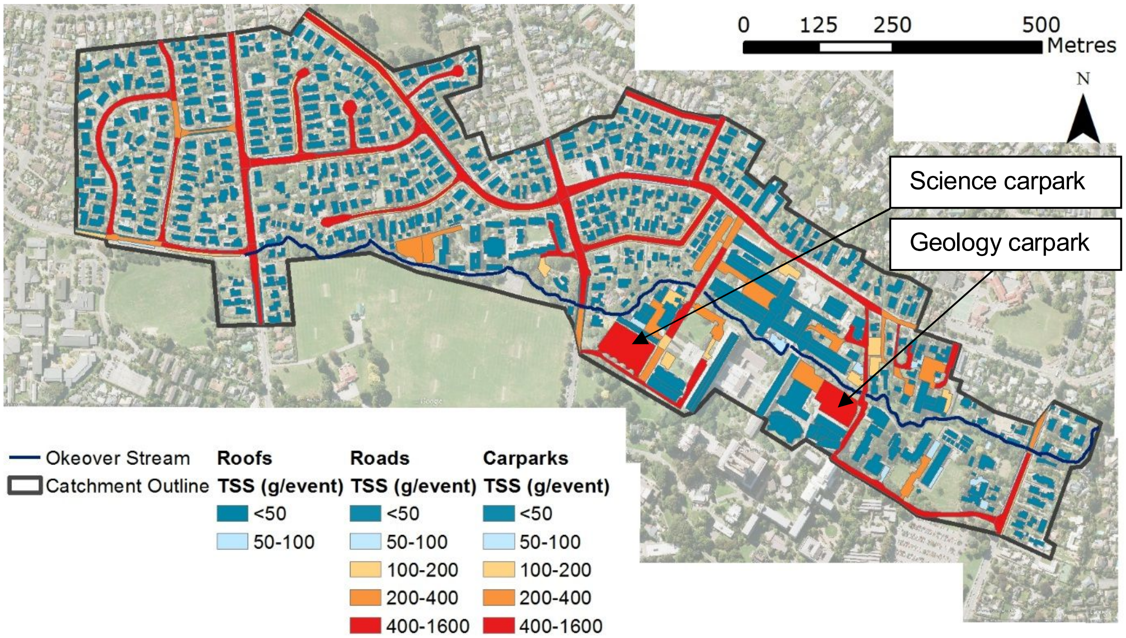


Figure 6-20: Average TSS event loads from individual surfaces in the Okeover catchment

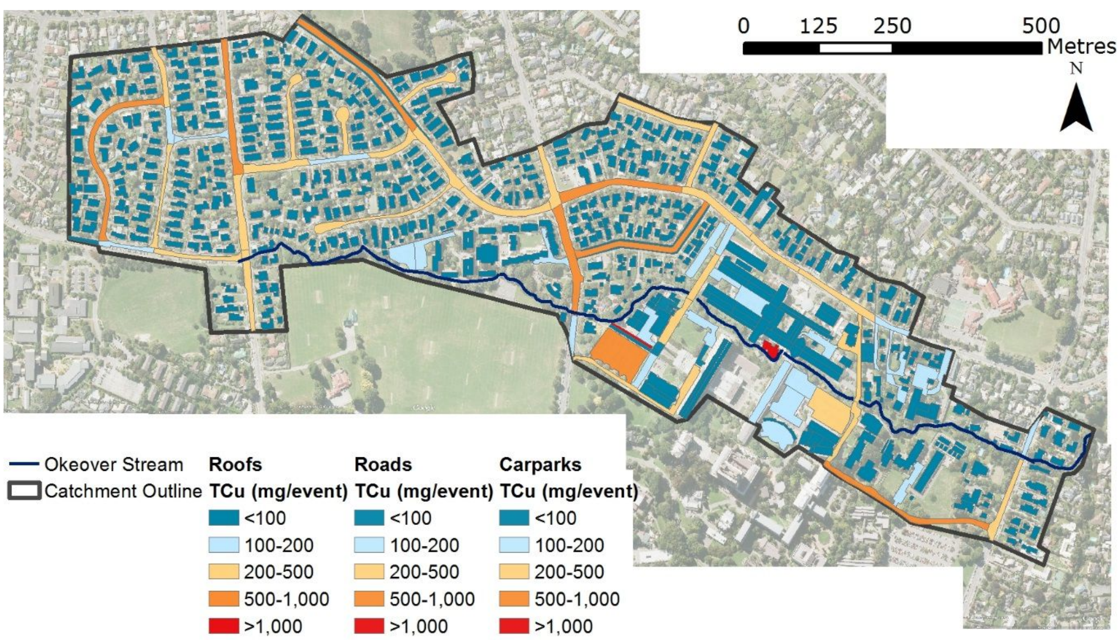


Figure 6-21: Average total copper event loads from individual surfaces in the Okeover catchment

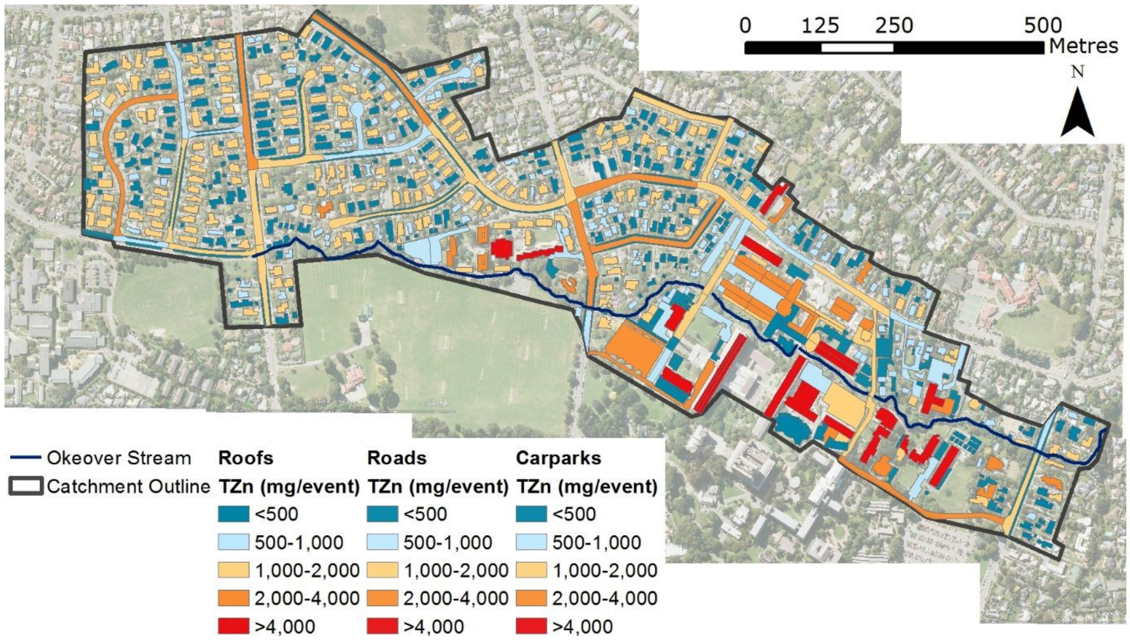


Figure 6-22: Average total zinc event loads from individual surfaces in the Okeover catchment

6.6 Discussion

6.6.1 Benefits of current model framework

As a generalised model that can be calibrated to a particular catchment using local runoff quality data, MEDUSA performed acceptably as a pollutant load model with NSE of at least 0.43 for TSS, 0.46 for copper and 0.63 for zinc. In contrast, the linear regression model can only be applied to the Okeover catchment and for rain events that are within the range (and combination) of event characteristics of the sampled rain events, which is a major restriction on the applicability of the LR model.

The MEDUSA framework also has the benefit of accommodating other pollutants. Other heavy metals of concern can be added using the existing heavy metal load equations by developing model coefficient values for these other metals from a monitoring dataset of pollutant loads and rainfall characteristics. Other pollutants such as nutrients would require a more extensive dataset to confirm what the most appropriate equation form is to simulate nutrient build-up and wash-off in relation to rainfall characteristics.

6.6.2 Limitations of current model framework

Representing physical processes

MEDUSA only predicts the pollutant loads as they are generated at each surface, and therefore does not account for changes in pollutant load as the runoff is conveyed through the stormwater network and is discharged in the receiving waterway. The presence of sumps, for example, may cause coarse sediment to settle out in the sump and be removed from the system during maintenance (e.g. vacuum cleaning of sumps). Any existing treatment systems in the modelled catchment will also remove targeted pollutants. Further research is needed to enable the incorporation of stormwater management options and pollutant transformation processes into the model framework. However, within its current scope, MEDUSA does allow stormwater managers to assess where and what surfaces should be targeted for improved stormwater management and the presence of existing treatment and maintenance practices can be taken into account as part of the planning to address those identified surfaces of concern.

Restricting the rainfall characteristics that each pollutant load is related to within the model framework can inadvertently cause false relationships to show in the interpretation of model coefficient values. For example, the calibrated TSS coefficient values for the MEDUSA model suggests that the copper roof was substantially more influenced by ADD than the concrete and galvanised roofs (i.e. higher ADD coefficient values; Table 6-15). However, because MEDUSA's framework is restricted to relating TSS loads to ADD only, it is likely that the high TSS loads from copper roofs are not due directly to ADD (patination is largely driven by water, carbon dioxide and time), but simply a means by which the model can reproduce high TSS loads. Furthermore, the NSE values of the calibrated MEDUSA model were lower for TSS than for metal predictions. While this suggests that a wider combination of rainfall characteristics could produce a better prediction of TSS event loads, the similarly lower NSE values for the LR model (which incorporated more rainfall characteristics in its TSS model) indicate that factors beyond rainfall characteristics are important drivers of TSS build-up and wash-off.

Model performance verification

As the available dataset for MEDUSA model calibration and LR model development was limited, the entire dataset was used for calibration instead of truncating the dataset for calibration and having a small validation dataset (following similar approaches by hydrologic modellers, for example Shrestha *et al.* (2016)). The models can be expected to perform reasonably for simulated events with rainfall characteristics within the ranges of the sampled events' characteristics; however, model performance may decrease when the simulated event characteristics fall outside these ranges.

Minimising model error and uncertainty

Model errors and uncertainties arise from conscious choices and simplifications made when developing model, such as limiting the number of input parameters to describe the complex pollutant build up and wash off process or using representative surfaces types and aggregating the specific characteristics of each roof within that surface type category. Uncertainties can also arise from potential unknowns though, hence the outputs taken as predicted values only. Various decisions were made in the development of both the model framework and the sampling dataset to minimise the scale of errors and uncertainty in the model (Table 6-20).

Table 6-20: Sources of errors and uncertainty in the model and untreated runoff dataset and minimisation methods used

Source	Description	Minimisation methods used
Data collection		
Sample sites	Limited number of surfaces characterised. It is assumed that each site is fairly typical and therefore representative of its type. Each sampled surface will have its own condition and characteristics that influence pollutant generation.	The research has focused on defining the key characteristic, surface material type, that drives pollutant generation. It is expected that variations within each surface type are less than the scale of the differences between different surface types.
Runoff sample collection technique	Coarser solids can readily settle if the runoff energy lessens; autosamplers have been found to preferentially abstract finer suspended sediments when placed in a stream.	This research's sampling technique of capturing the majority, if not all, the flow coming out of a downpipe or overflowing into a sump has minimised errors associated with not capturing a representative sample from the water column.
Rainfall assumptions	A single weather station has been used to provide rainfall characteristics for all sampled surfaces.	All surfaces are within 300 m of the weather station, so variation in rainfall expected to be very limited.
Defining samples as FF, transitional or SS samples	There is variation in the time of concentration for each droplet falling on the road to reach the sump; SS conditions had concentrations within a relatively consistent range however, there was still variation in concentration between adjacent SS samples because of fluctuations in intensity etc.	Sampled surfaces were kept relatively small to minimize differences in time of concentrations and therefore arrival of first flush at the sampling point. The variance in SS samples was distinctly less than any difference observed between the scale of FF and SS concentrations for each site.
Lab analysis		
Methods	Potential for subsampling to capture non-representative sample quality	Used internationally accepted methods; used whole sample bottles for TSS to minimise subsampling effects.
Machine/instrumentation limits	Each method has limits of detection (upper and lower bounds) that it can provide an appropriately accurate reading within. It also has accuracy limits for any given reading value (e.g. ± 5%)	Ensure they were set for appropriate range. ICPMS uses extensive standards checks and regular calibration across a range of metal concentration levels.

Source	Description	Minimisation methods used
Process representativeness		
Representing wash off processes	The derivation of observed event loads assumes there is no significant evaporation or soakage occurring on the surface that causes a loss of rainfall volume (and therefore rainfall depth can be used as a surrogate for per area runoff volume).	As runoff flows would have been very difficult to accurately measure from a downpipe or into a sump without interfering with the ability to get whole-of-flow samples, this error has been accepted. As the rain in Christchurch is typically caused by a cold front or slow-moving onshore system where there is significant cloud build-up prior to start of rain, the surfaces temperatures are not expected to be particularly elevated.
Predictor variables	The Addington results demonstrate that more parameters (beyond rainfall characteristics) are needed to adequately predict copper for example, as the model fit is relatively poor.	For most surfaces, a good fit could be found indicating that the selection of rainfall characteristics and categorisation by surface material into the model framework capture a significant amount of the drivers for pollution generation.
Calibration process		
Limited dataset	More data is always needed; Addington served as a kind of verification for the model's ability to be applied to different catchments. More verification data is needed for the same surface types as sampled in the Okeover catchment to further test model calibration performance.	A more robust calibration has been achieved by using the full dataset for calibration, however, this has come at the expense of being able to validate the model with this dataset. A validation dataset is being developed from further untreated runoff sampling (outside this PhD research scope).

6.6.3 Influence of rainfall characteristics on heavy metal loads

For the total copper MEDUSA model, the copper roof was substantially more influenced by rainfall pH than the other two roof surfaces, and to a lesser extent, by average rainfall intensity. For the total zinc MEDUSA model, the galvanised roof was more influenced by rainfall pH (particularly during steady state conditions) than the other two roof surfaces. It was also more influenced by ADD and to a lesser extent average rainfall intensity.

Only one rainfall variable, log-transformed rainfall depth, was found to be a common factor amongst all TSS, total copper and total zinc linear regression models for all surface types. The sole exception where depth was not included as a variable in the best-fit model was the zinc model for road runoff. Log-transformed ADD was a common variable for most of the copper and zinc models. Good predictive models were found for dissolved copper and zinc using only the total metals loads as the predictor variable. This suggests that although rainfall pH and sediment availability could be expected to influence the partitioning of metals between particulate and dissolved, in the untreated runoff, at least, the metals partitioning is relatively consistent.

The MEDUSA model assumes rainfall pH is a significant variable relating to both initial and steady state copper concentrations, and the initial concentrations are also dependent on ADD and average intensity (see Table 6-14 for summary of reported rainfall influences on pollutant generation). The dataset used to inform the linear regression models ranged in rainfall pH from 5.1 to 7.9, which does not allow characterisation of the pollutant load's response to broader changes in pH, and may explain why no relationship to rainfall pH was seen in the linear regression models for either road or roof runoff (with the sole exception of the TZn LR model for road runoff). Therefore, for application of the model in a catchment that does not have acid rain or where copper roofs are not a concern, the linear regression model results suggest that rainfall pH is not a significant influence on metal loads in runoff.

6.6.4 Comparison of literature-derived coefficient values to Okeover-calibrated values

There are substantial differences in the Okeover-calibrated model coefficient values compared to those derived from literature (refer to Appendix H), which confirm the need to calibrate the model to local rainfall characteristics. A low intensity rainfall climate such as Christchurch's shows a different sensitivity to ADD, intensity and pH, where the literature-derived values have largely been from studies under simulated rainfall conditions. The Okeover-calibrated model coefficients also recognise the contribution of heavy metals from all roof surface types, not just copper from copper roofs and zinc from zinc-based roofs. This acknowledges the contribution, albeit small, of these metals via atmospheric deposition, and is important for more effectively identifying the cumulative load contribution from these surfaces.

6.6.5 Model application

The model was able to identify which individual surfaces are producing the highest range of event loads within the catchment. The comparison of MEDUSA predicted loads to the LR model's predicted loads for the year 2012 events in the Okeover catchment demonstrate the limitations of a catchment-specific model when applied to different rain events where the combination of rainfall characteristics fall outside those of the dataset that the LR model was trained with. The LR model was found to consistently predict heavy metal loads orders of magnitudes below the range seen in the sampled event loads (and therefore considered not very likely), or predict extraordinarily high metals loads from individual surfaces.

The sampling dataset used to calibrate the model and apply it to the Okeover catchment was restricted to four impermeable surface types, albeit the most common types found in the catchment. Therefore, assumptions had to be made to assign model coefficient values to all surface types present in the catchment that differed from the four sampled surface types. Further monitoring is needed of untreated runoff from different surface types, particularly carparks, unpainted galvanised roofs and new painted Zincalume® roofs (e.g. Coloursteel ®) to enable the calibration of model coefficients for a wider range of surface types.

6.7 Conclusions

A pollutant build-up and wash-off model, MEDUSA, was developed to predict TSS and total dissolved copper and zinc event loads for individual impermeable surfaces. Rainfall characteristics were used in the model as the independent (predictor) variables. The model was calibrated to the low intensity rainfall conditions found in Christchurch, New Zealand, using a dataset of untreated runoff quality, as described in Chapters 3 and 4. MEDUSA was found to be most effective at predicting total zinc loads (NSEs of 0.63-0.73), and was still reasonably effective at predicting total copper loads (NSEs of 0.46-0.66) and sediment loads (NSEs of 0.43-0.74 for roofs). MEDUSA was noticeably more effective at predicting pollutant loads from road surfaces in comparison to concrete, copper or galvanised roof surfaces.

The variation in the calibrated model's coefficient values between each surface type confirms that it is necessary to apply pollutant load models at an individual surface scale rather than a catchment or land use scale. The good performances of the metal models also reinforce the appropriateness to use specific relationships for each pollutant, rather than assume metal loads are proportional to sediment loads for every event and surface type. This is especially important for impervious metallic surfaces, such as copper or galvanised roofing, where direct dissolution of the metals is a key process for pollutant generation.

MEDUSA was also compared against linear regression models that were developed using the same dataset that was used for calibrating MEDUSA. The aim was to compare the performance of MEDUSA as a calibrated but generalised process model with a catchment-specific linear regression model. Linear regression models were effective for predicting TSS loads (NSEs of 0.66-0.90), total copper loads (NSEs of 0.85-0.91) and total zinc (NSEs of 0.82-0.94). MEDUSA was consistently less effective at predicting pollutant loads, although its NSE values are all moderate to strong. Furthermore, when both MEDUSA and the LR model were applied to the Okeover catchment as a case study, it became apparent that the LR model is less robust in its load predictions when the model is applied to different rain events outside the combination of characteristics of the sampled events that were used to train the model.

In terms of how the model outputs can be used to help guide stormwater management decision-making and planning, MEDUSA clearly identified the spatial distribution of the generation of each pollutant within the catchment. MEDUSA was able to identify where the highest average event loads were being produced; it clearly showed that roads and two large carparks within the University are the key contributors of sediment, and should be targeted for sediment reduction through stormwater treatment. Conversely, while roads and carparks are generating elevated total copper loads, the loads from a small area of copper roofs on the University grounds are generating disproportionately high copper loads. This suggests that copper roofing material should be avoided or replaced within a catchment to effectively limit or reduce copper pollution from stormwater. Large galvanised roofs (primarily within the University) were shown to be the key contributors of zinc.

7 Pollutant Load Model Application Case Study: Addington Brook Catchment

7.1 Introduction

Following the development of a calibrated version of the MEDUSA model for the Okeover Catchment (refer to Chapter 6 for further details), MEDUSA was recalibrated and applied to a second catchment in Christchurch. The aim was to assess the feasibility of recalibrating and applying the model to a different catchment while producing reasonable predictions of pollutant loads. The Addington Brook catchment was selected as previous instream water quality modelling has shown elevated copper, lead and zinc (Stevenson & Margetts 2015), with samples taken during stormflow conditions generally showing the highest pollutant concentrations, confirming that stormwater is a key contributor of these pollutants.

This chapter's structure differs from the rest of this thesis in that it details the whole process of implementing the MEDUSA model, from data collection and analysis to model calibration and simulation. The process used for the Addington application aimed to optimise the sample collection and calibration process to reduce sampling and analysis costs while achieve robust modelling results. This application also demonstrates how MEDUSA can be used to predict a range of different load metrics including event loads, seasonal loads and annual loads as well as predicted loads for specific design storms.

7.2 Addington Brook catchment description

Addington Brook is a stormwater-influenced brook that headwaters in western Christchurch. It passes through a combination of modified open drainage channels, short culverts and extended piped sections to reach South Hagley Park. It then passes through the park in an open channel and joins the Avon River/Ōtākaro near the Christchurch Hospital (Figure 2-1).

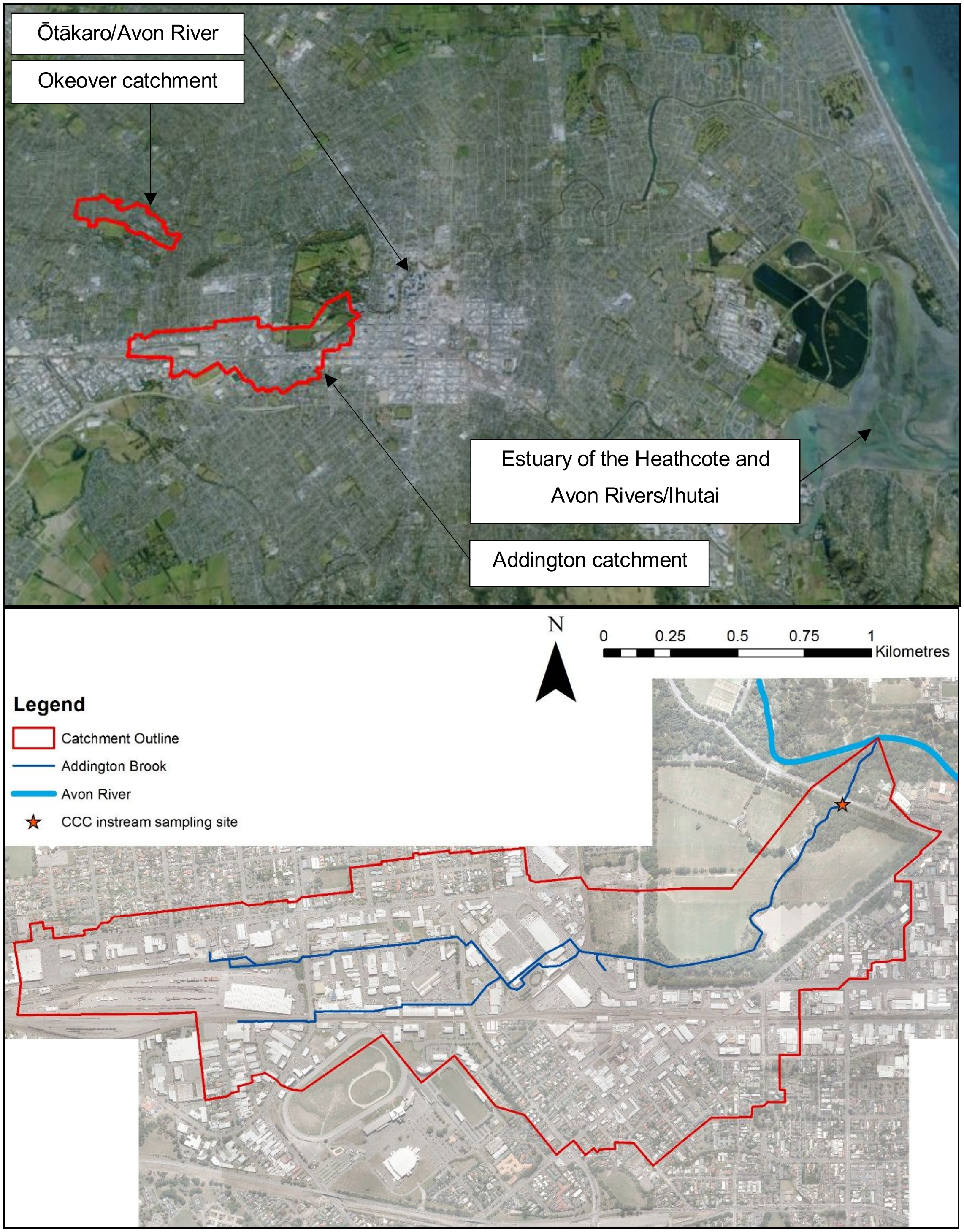
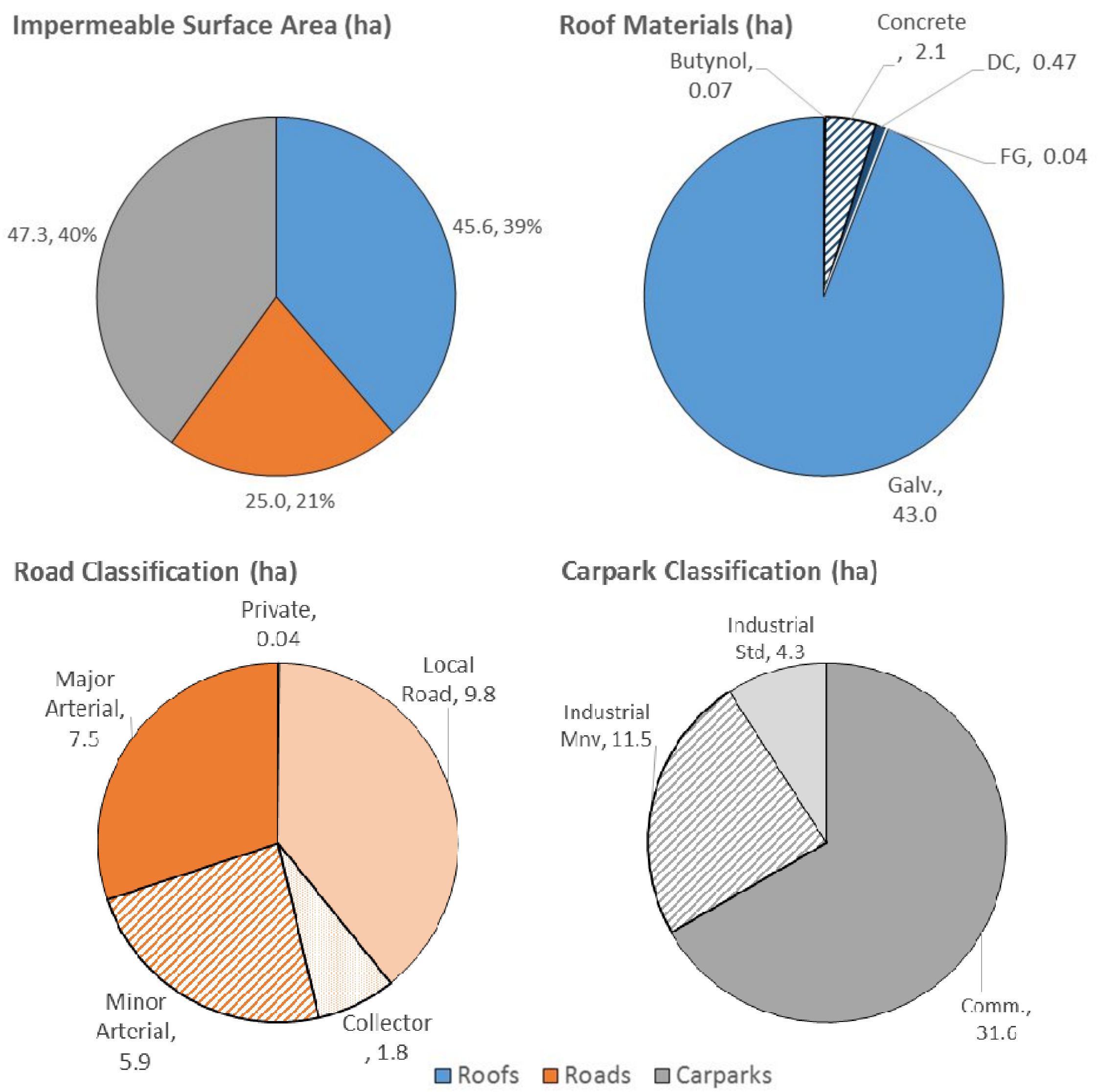


Figure 7-1: Location map of Addington Brook catchment and nearby Okeover Stream catchment in Christchurch

The Addington Brook catchment consists of 243 ha of mixed industrial, commercial and residential land use. The vast majority of its roof surfaces are galvanised, many unpainted in the industrial/commercial areas, although some newer roofs in both the industrial/commercial and residential areas are painted or powder-coated (e.g. Coloursteel®) (Figure 7-2). Over half the roads passing through the catchment are either minor or major arterial roads (typical total daily traffic flows of 3,000-15,000 and >12,000, respectively) (Figure 7-2). Most carpark surfaces in the catchment are commercial; of the remaining industrial carparks, the majority are used by slow-moving, manoeuvring heavy vehicle traffic (hereafter referred to as 'Industrial Manoeuvring' carparks).



Roofs - DC: decramastic tiles; FG: fibreglass; Galv.: galvanised. Carparks - Comm.: commercial

Figure 7-2: Composition of impermeable surfaces by material type in Addington catchment

7.3 Methodology

7.3.1 Sampling sites

Seven sites were monitored for first flush (FF; for the purposes of this study defined as the first 1 L of runoff) and steady state runoff quality (Table 7-1, Figure 7-3). The sites were considered representative of the most common surfaces types in the catchment. Priority was given to sampling a wide range of surface type and conditions to further enhance the calibration of MEDUSA, as the data would allow model coefficient values to be calibrated for more surface types (than could be done with the four Okeover sampled surfaces).

Table 7-1: Sampling site characteristics

Site	Site Code	Surface type	Description	Estimated Drainage Area (m^2)
GoBus carpark	GBC	Chipseal carpark	Coarse chipseal; bus traffic	1,170
GoBus downpipe	GBD	Unpainted galvanised roof	Old unpainted galvanised roof	220
Kiwirail carpark	KRC	Asphalt carpark	Smooth asphalt; heavy vehicle traffic	2,900
Lincoln Road sump	LNR	Asphalt road	Smooth asphalt; primarily car traffic, limited heavy vehicle traffic; runoff from Lincoln Road 19,200 AADT	150
Picton Avenue sump	PCR	Asphalt road	Smooth asphalt; cars and significant heavy vehicle traffic; runoff from Blenheim Road 40,700 annual average daily traffic (AADT)	1,120
Tower Junction carpark	TJC	Asphalt carpark	Smooth asphalt; car traffic	150
Tower Junction downpipe	TJD	Unpainted galvanised roof	Brand new (<1 year old) unpainted GalvSteel® roof	440

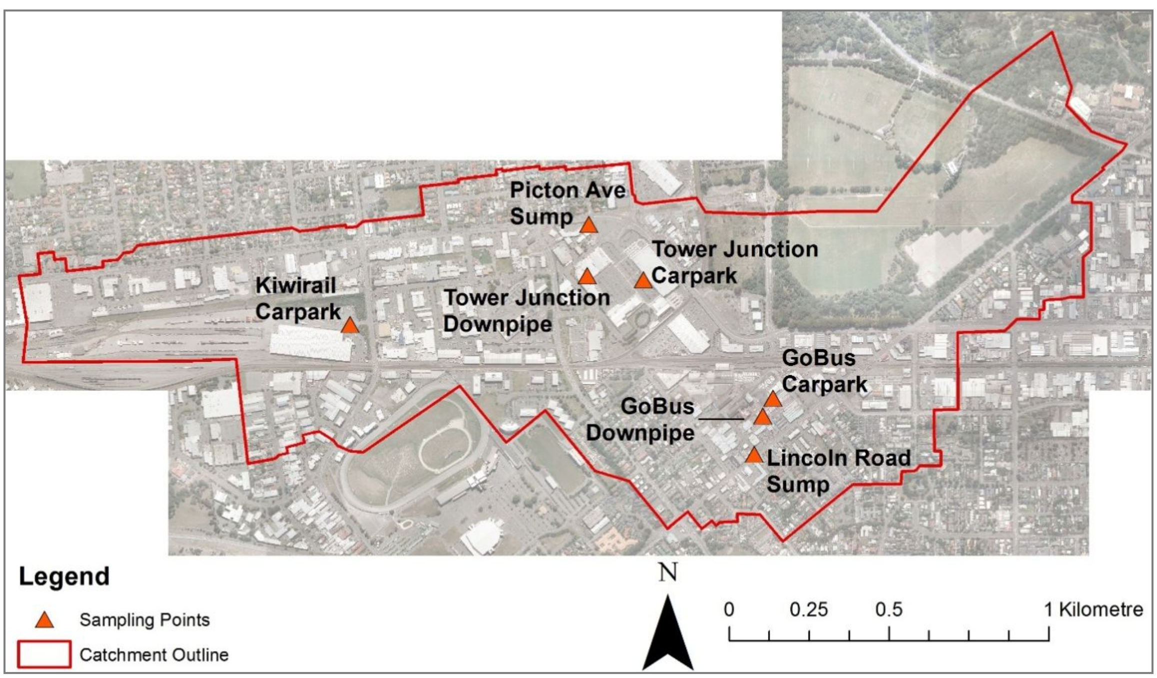


Figure 7-3: Location map of sampling sites in Addington Brook catchment

7.3.2 Sample collection

Runoff samples were collected from 9 rainfall events between mid-September and mid-December 2015. A minimum of 4 FF and 5 SS samples were collected from each site (Table 7-2).

Table 7-2: Record of samples collected

Sampling Site	Site Code	FF samples	SS samples	Total no. of samples
GoBus carpark	GBC	7	6	13
GoBus downpipe	GBD	8	5	13
Kiwirail carpark	KRC	8	6	14
Lincoln Road sump	LNR	6	4	10
Picton Avenue sump	PCR	5	4	9
Tower Junction carpark	TJC	6	5	11
Tower Junction downpipe	TJD	5	4	9

An optimised sampling procedure was used in the Addington catchment, which resulted in the collection of a single FF and a single SS sample (when possible) for each event. This optimised procedure reduced sampling costs and time associated with sampling. However, it required additional assumptions to be made on the pollutant concentration responses for the estimation of event pollution loads, as follows:

- *Consistent steady state concentrations are achieved in each rain event:* this is a reasonable assumption based on the observations of steady state concentrations from the more extensive Okeover sampling dataset.
- *The pollutant concentration change from FF to SS can be approximated as a linear rate*: Again, the time-series data from the Okeover dataset suggest this assumption is appropriate.

Thermo Scientific™ Nalgene™ Storm Water Sampler bottles (1 L HDPE) were used to collect FF samples. For carpark and road runoff sites, they were deployed by suspending the bottle from the sump grate with a cable tie, in the corner of the sump where the initial runoff would flow in (Figure 7-4). For the Tower Junction downpipe, the bottle was suspended via cable tie from a leaf guard into the top of the downpipe. For the GoBus downpipe, the bottle was fitted within a Thermo Scientific™ Nalgene™ Storm Water Mounting Kit and fixed under the downpipe (Figure 7-4). The use of these bottles allowed the collection of FF samples where it was logistically impossible to take FF grab samples at all 7 sites or when the rain started after dark.

Figure 7-4: Examples of sampling set up at Addington sites (From left: Mounting kit within FF sampler bottle inside fitted to downpipe; FF sampler bottle deployed in carpark sump; runoff entering carpark sump during SS conditions (grab sample taken at point x))

Grab sampling (1 L HDPE) was used for all steady state samples, restricting any SS sampling to daylight hours. Full FF bottles were picked up at the time of SS sampling (or as soon as possible after FF, i.e. first thing the next morning). All samples were taken directly to an International Accreditation New Zealand (IANZ) accredited lab, Hill Laboratories, for analysis (within 24 hours of collection). Samples were transported during collection and delivery in an insulated container with icepacks.

7.3.3 Quality control

Preparation of sampling bottles

The FF sampler bottles were cleaned and acid washed prior to each use (as per the Okeover sampling containers). Following each sampling event, all SS sampling containers were replaced with fresh ones for the subsequent sampling event.

Sample preservation

FF sampler bottles were decanted into 1 L unpreserved HDPE containers for delivery to the lab, with care taken to ensure all sediment was transferred from the FF bottle into the container. For Event 1, the samples were taken to the University of Canterbury EEL for sample preservation as Hill Laboratories was closed for the day and the samples could not be delivered until the following morning. The total metal samples were preserved with concentrated (69%) nitric acid (Fisher, trace analysis grade) to reduce the pH to less than 2.0 (APHA, 2005). Dissolved metal samples were pre-filtered through disposable Waterra 0.45 μm filters before preservation with nitric acid.

For all subsequent events, the samples were able to be delivered immediately to Hill Laboratories after collection and therefore, the samples were provided to Hill Laboratories in 1 L unpreserved HDPE containers.

7.3.4 Laboratory analysis

Table 7-3 summarises the analytical methods used by Hill Laboratories on all samples.

Table 7-3: Analytical methods and limits of detection

Water quality parameter	Analytical method	Method description	Limit of detection
TSS	APHA 2540 D	Filtration using nominal pore size 1.2-1.5 µm, gravimetric determination	3 g/m^3
Total metals	APHA 3125 B	Nitric acid digestion, filtered through 0.45 µm, ICP-MS (trace level)	Copper – 0.00053 g/m^3 Lead – 0.00011 g/m^3 Zinc – 0.0011 g/m^3
Dissolved metals	APHA 3125 B	Filtered through 0.45 µm, ICP-MS (trace level)	Copper – 0.0005 g/m^3 Lead – 0.00010 g/m^3 Zinc – 0.0010 g/m^3

7.3.5 Sampled event rainfall characteristics

Weather data collection

Average and 5-minute peak rainfall intensity, event duration and length of the antecedent dry period were recorded for each event using meteorological data from the National Institute of Water and Atmosphere's (NIWA) Kyle Street Weather Station, located 500 m north of the Addington catchment boundary. Rainfall was collected and pH measured for each event during SS sample collection. Where the rain occurred overnight, the rainfall pH was measured from a wet deposition sampler on the roof of University of Canterbury's Department of Civil and Natural Resources Engineering building (approximately 2.5 km NW of the Addington sampling sites).

Sampled event characteristics

The sampling period from mid-September to mid-December 2015 was unusually dry, with monthly rainfalls in October and November at 23% and 63%, respectively, of the average monthly rainfall (NIWA 2015b, c). The partial sampling periods in September and December had more typical rainfall (NIWA 2015a). Nevertheless, 9 events were sampled, with median and range of values of rainfall characteristics provided in Table 7-4. Due to sampling logistics, not all surfaces could be sampled for every event, however all seven sites were sampled during Events 5, 7, 8 and 9.

Average intensity, peak intensity and duration all showed left-skewed distributions, while the other rainfall characteristics were more evenly spread. All sampled events were within the 50% annual exceedance probability (AEP) for a rainfall event in the catchment, as predicted by the High Intensity Rainfall Design System Version 3 (HIRDS.V3) (NIWA 2011) (Figure 7-5).

Table 7-4: Sampled rainfall event characteristics

Event No.	Start Date	Rainfall pH (S.U.)	Average intensity (mm/hr)	Peak 5-min intensity (mm/hr)	Antecedent dry period (days)	Duration (hrs)	Depth (mm)	Depth of preceding event (mm)	Sites sampled [1]
1	10 Sep 2015	6.98	1.82	9.36	4.49	4.6	8.34	0.32	GBC, KRC
2	18 Sep 2015	6.20	0.86	2.16	1.50	0.8	0.72	0.50	GBC, GBD, KRC, TJC, TJD
3	22 Sep 2015	6.46	0.86	5.28	1.10	19.0	16.26	0.50	GBC, GBD, KRC, TJC
4	22 Oct 2015	6.52	0.45	0.84	3.95	0.7	0.30	1.10	GBC, GBD, KRC, LNR, PCR
5	28 Oct 2015	6.67	0.97	4.20	6.15	4.9	4.79	0.30	All 7 sites
6	3 Nov 2015	6.71	0.35	2.28	5.78	0.9	0.32	2.01	GBD, KRC, LNR, TJC, TJD
7	11 Nov 2015	6.82	0.51	5.64	3.19	18.5	9.40	0.60	All 7 sites
8	6 Dec 2015	5.67	0.20	0.96	2.16	6.4	1.26	1.40	All 7 sites
9	13 Dec 2015	5.69	3.87	31.56	5.65	3.3	12.90	2.20	All 7 sites
Median		***6.52***	***0.86***	***4.20***	***3.95***	***4.6***	***4.79***	***0.60***	
Minimum		***5.67***	***0.20***	***0.84***	***1.10***	***0.7***	***0.30***	***0.30***	
Maximum		***6.98***	***3.87***	***31.56***	***6.15***	***19.0***	***16.26***	***2.20***	

[1] GBC: GoBus carpark (industrial); GBD: GoBus downpipe (old galvanised roof); KRC: Kiwirail carpark (industrial); LNR: Lincoln Road sump (minor arterial road); PCR: Picton Ave sump (major arterial road); TJC: Tower Junction carpark (commercial); TJD: Tower Junction downpipe (new galvanised roof)

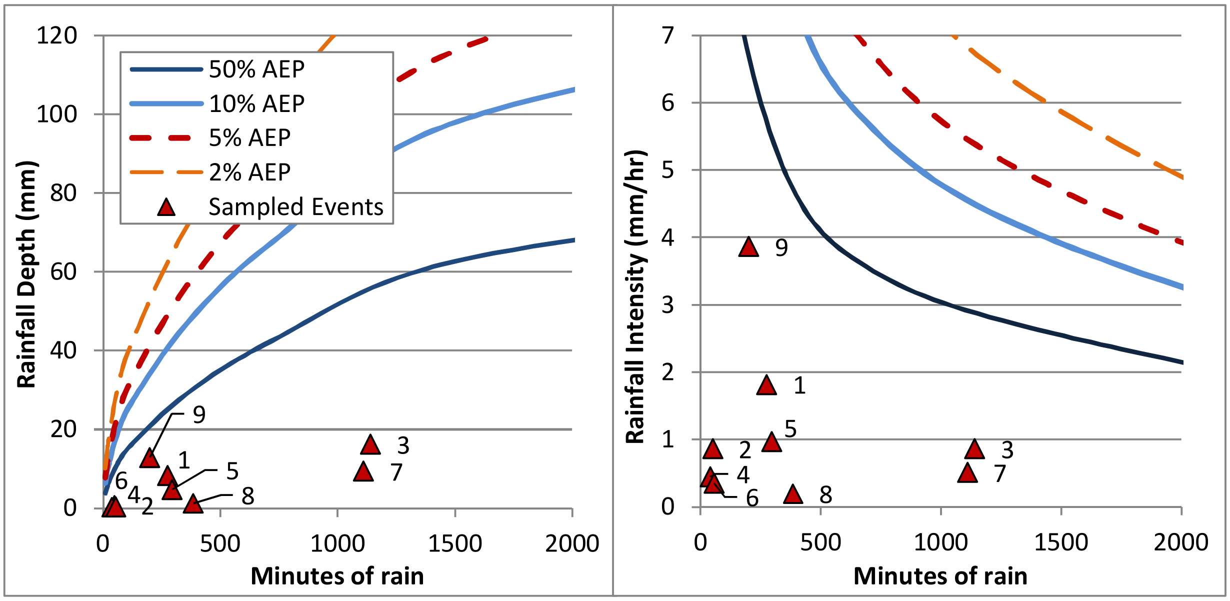


Figure 7-5: Depth versus duration (left) and average intensity versus duration (right) of sampled rainfall events against HIRDS predicted annual exceedance probability curves for the Addington catchment

7.3.6 Derivation of pollutant loads from sampled Addington data

The sampled dataset of untreated runoff was used to calculate total event pollutant loads (L; mg/m^2/event or µg/m^2/event) for each sampled surface. The event loads were calculated on a per area basis using the measured FF and SS pollutant concentrations, assuming an approximated linear decay from FF to SS over the transition time, Z, as follows:

$$L = \frac{\frac{C_{FF}-C_{SS}}{2}Z + C_{SS}(DUR-Z)}{DUR} \times DEPTH \tag{7-1}$$

where

where	C_{FF}	first flush pollutant concentration	(mg/L or µg/L)
	C_{SS}	steady state pollutant concentration	(mg/L or µg/L)
	Z	transition time	(mins)
	DUR	duration	(mins)
	$DEPTH$	total event depth	(mm)

The value of *Z* was taken as 0.75 hours, based on observations from the Okeover sampling where time-series sampling enabled derivation of a representative transition time value (refer to Chapter 4: Section 4.3.4). These loads derived from the observed concentrations (hereafter, the observed loads) were then compared against model predicted pollutant loads to assess model predictive performance.

7.3.7 Recalibration of MEDUSA model to Addington data

Overview of calibration methods

Three calibration options were evaluated for the Addington MEDUSA model, as follows:

1. *Application of Okeover-calibrated model coefficient values directly to the Addington sampled surfaces*: This option assumes that surfaces sampled in the Okeover catchment are sufficiently similar to the sampled Addington surfaces that the same model coefficient values can be used for new surface types that were sampled in the Addington catchment (but had not been sampled in the Okeover).
2. *Application of a scalar multiplier unique to each surface type to the loads predicted using the Okeover-calibrated model coefficients*: This option assumes that the relationship of pollutant build-up and wash-off processes to rainfall characteristics are fundamentally consistent between similar surface types (e.g. the Okeover's galvanised roof and the two galvanised roofs sampled in the Addington catchment). Therefore, a scalar multiplier (i.e. a linear correction) can be applied to the predicted loads to account for changes in atmospheric deposition rates or increased traffic intensity, for example.
3. *Recalibration of model coefficients to achieve optimised NSE values:* This option assumes that the pollutant build-up and wash-off processes are unique for each surface type and expands upon the calibrated surface types that were developed for the Okeover MEDUSA model as the Addington sampling data gathered runoff from additional surface types not characterised in the Okeover sampling dataset.

Calibration Method 1: Okeover-calibrated model coefficient values

Under this option the seven sampled surfaces were restricted to being characterised as one of two similar sampled surfaces from the Okeover (Table 7-5; refer to Table 6-18 for details of Okeover sampled surfaces).

Table 7-5: Classification of Addington surfaces using Okeover-calibrated model coefficients

Surface type	Addington sampled surface	Source of model coefficients
Roofs	Tower Junction downpipe (New unpainted galvanised roof)	Okeover galvanised roof
	GoBus downpipe (Old unpainted galvanised roof)	Okeover galvanised roof
Roads	Lincoln Road sump (Minor arterial road)	Okeover asphalt road
	Picton Ave sump (Major arterial road)	Okeover asphalt road
Carpark	Tower Junction carpark (Commercial)	Okeover asphalt road
	GoBus carpark (Industrial Manoeuvring)	Okeover asphalt road
	Kiwirail carpark (Industrial Standard)	Okeover asphalt road

Calibration Method 2: Scalar multiplier values

Scalar multiplier values were derived from the average ratio of the load predicted for the surface using Okeover-calibrated values (i.e. Calibration Method 1 predicted load values) against the observed loads, to evaluate whether a simple linear adjustment could be made to achieve a better model fit than Calibration 1, but without the time required to recalibrate all model coefficient values (i.e. Calibration Method 3).

Calibration Method 3: Recalibration of model coefficient values

This method follows the same calibration method used for the Okeover model application (Chapter 6). As there was now additional runoff characterisation data from the seven Addington sampled surfaces that could be combined with the four Okeover sampled surfaces, a more detailed classification of the impermeable surface types was developed for roof, road and carpark surface types (Table 7-6).

Table 7-6: Surface type classifications derived for the Addington MEDUSA model

Surface type	Classification	Related sampled surface
Roof	Butynol All	MEDUSA standard neutral (non-metallic) roof surface (parameters derived from sampled concrete roof runoff in the Okeover catchment)
	Decramastic All	
	Concrete All	
	Fibreglass All	
	Galvanised New (or painted moderate condition)	Okeover painted galvanised roof
	Galvanised Moderate	Tower Junction downpipe
	Galvanised Old	GoBus downpipe
Road	Private	MEDUSA standard asphalt road surface (parameters derived from sampled asphalt road runoff in the Okeover catchment)
	Local	
	Collector	
	Minor arterial	Lincoln Road sump
	Major arterial	Picton Avenue sump
Carpark	Commercial	Tower Junction carpark
	Industrial Manoeuvring (Heavy vehicles manoeuvring (stops, starts, turns) regularly across surface)	GoBus carpark
	Industrial Standard (Heavy vehicles presence but less slow manoeuvring)	Kiwirail carpark

7.4 Untreated runoff quality results

The highest TSS loads were found at the carpark road sites (Table 7-7), followed by the road sites. The old galvanised roof had a very high first flush TSS but the lowest steady state TSS concentration of any site. Total copper concentrations showed a similar pattern to TSS, suggesting that copper may come from the same source as much of the sediment on these surfaces. The two galvanised roofs produced substantially more zinc than any of the other surfaces, with the old galvanised roof producing extremely high zinc concentrations that exceed values reported elsewhere in literature (refer to Chapter 2: Section

2.2.4). Almost all the zinc from the galvanised roofs was in dissolved form (Figure 7-6). Both the old and new unpainted roofs were higher than the concentrations produced by the painted (but ~15 years old) galvanised roof in the Okeover catchment. In general, FF pollutant concentrations were consistently higher than the SS concentrations for the same event, for every sampled surface.

Table 7-7: Average pollutant concentration (and ranges) in Addington (with related surface data from the Okeover catchments)

Pollutant		Galvanised roof surfaces			Asphalt road surfaces			Carpark surfaces		
		Addington: old unpainted galvanised roof (Site GBD)	Addington: new unpainted GalvSteel® (Site TJD)	Okeover: ~15 yrs old painted galvanised roof	Addington: Major arterial road (40,700 AADT; Site PCR)	Addington: Minor arterial road (19,200 AADT; Site LNR)	Okeover: Collector road (11,000 AADT)	Commercial carpark (Site TJC)	Industrial carpark (Standard; Site KRC)	Industrial carpark (Manoeuvring; Site GBC)
TSS (mg/L)	FF	458 (184-820)	68 (29 - 127)	12 (1- 22)	240 (58-520)	289 (70-450)	155 (8-327)	305 (120-730)	447 (96-1,400)	516 (290-990)
	SS	3 (1.5-8)	20 (4 - 36)	2 (0.1-9)	103 (16-240)	43 (31-55)	49 (7-157)	34 (7-73)	84 (14-128)	78 (26-176)
Total copper (ug/L)	FF	78 (22-134)	35 (11-61)	9 (5-13)	99 (51-153)	129 (73-230)	54 (7-84)	94 (52-141)	92 (29-127)	176 (65-330)
	SS	3 (2-5)	16 (7-34)	5 (3-9)	42 (23-55)	20 (9-45)	20 (7-52)	19 (9-24)	23 (6-35)	55 (21-103)
Dissolved copper (ug/L)	FF	7 (2-14)	13 (1-22)	4 (2-13)	38 (9-56)	26 (14-47)	17 (2-32)	42 (13-58)	36 (7-74)	61 (11-153)
	SS	0.8 (0.3-1)	5 (3 -7)	2 (0.2-8)	16 (6-29)	20 (9-45)	5 (1-12)	11 (6-23)	7 (1-16)	33 (8-93)
Total zinc (ug/L)	FF	32,338 (11,700-56,000)	4,782 (410-12,600)	1,005 (372-2,369)	1,480 (950-1,950)	1,393 (520-2,400)	222 (26-429)	822 (190-1,760)	1,584 (490-2,600)	800 (320-1,550)
	SS	5,920 (2,400-8,700)	1,085 (940-1,120)	335 (75-1,057)	738 (490-1,080)	407 (137-700)	86 (20-203)	151 (108-200)	425 (130-850)	198 (98-320)
Dissolved zinc (ug/L)	FF	28,250 (10,700-53,000)	4,442 (410-11,400)	993 (372-2,369)	732 (400-980)	677 (220-1,730)	60 (21-98)	348 (190-460)	533 (76-1,130)	337 (59-760)
	SS	5,900 (2,300-8,700)	1,018 (940-1,120)	332 (75-1,057)	505 (210-1,100)	305 (81-460)	46 (12-78)	96 (81-134)	165 (37-420)	111 (38-220)

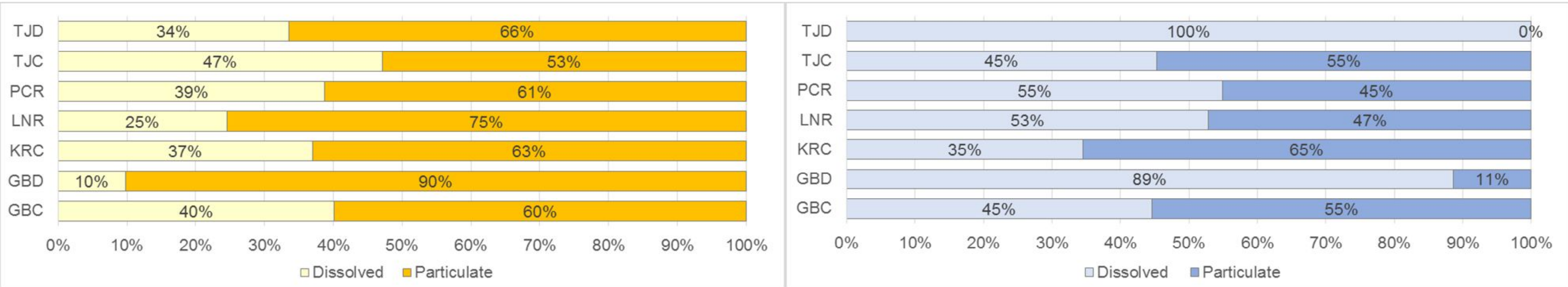


Figure 7-6: Average copper (left) and zinc (right) partitioning between dissolved and particulate form at each Addington sampling site

7.5 Model results

Derived calibration values

The Okeover-calibrated model coefficient values for each surface in Addington (Table 6-18) were used directly for Calibration Method 1 (refer to Chapter 6: Section 6.4.1). The scalar multiplier values used for Calibration Method 2 are summarised in Table 7-8, with suggestions given for how the scaling values reflect differences in pollutant sources and surface characteristics of the Addington surfaces in comparison to the Okeover surfaces. The recalibrated coefficient values (i.e. Calibration Method 3) are provided in Table 7-9. All three calibration methods were applied to the model and their performance compared.

Correlation of model predicted values to observed loads

The modelled load correlations resulting from Calibration Method 1 were generally high (i.e. the model predicted low loads for events where low loads were observed, and predicted high loads for events with high observed load), however the overall fit is poor with a wide scatter of predicted vs observed points (Figure 7-7 to Figure 7-11). In particular, this model version consistently under-predicted dissolved copper and zinc loads. Model predicted loads developed using either Calibration Method 2 or Calibration Method 3 show a markedly better fit to the observed loads than Calibration Method 1. The correlation is generally good for both low and high loads and there is substantially less scatter.

The NSEs of the Calibration Method 2 and 3 models are moderate to high for TSS, total copper and total zinc predictions, with exceptions being prediction of the GoBus carpark total copper (model predicted values worse than using mean as predictor) and the Lincoln Road sump total zinc (low NSE value only) (Table 7-10). The NSE values for these parameters from both calibration methods are very similar.

All versions of the model had difficulty in effectively predicting dissolved copper from all three carpark surfaces and the Picton Avenue road runoff site. Predictions of dissolved zinc were good for the roof runoff and commercial carpark sites, however, all versions of the model were very poor at predicting the dissolved zinc loads from the road sites (NSEs <0) and poor at predicting dissolved zinc from the industrial carpark sites.

The simpler Calibration Method 2 sometimes achieved higher NSEs values than the more complex Calibration Method 3, however, this is typically seen in the pollutants that are predicted based on their proportionality with another predicted pollutant (e.g. prediction of road heavy metals based on road TSS, prediction of dissolved metals from total metals).

Table 7-8: Calibration Method 2 - Scalar multipliers used to adjust Okeover-calibrated model predicted loads to Addington observed loads

Surface	Scalar multiplier					Influencing factors for Okeover-Addington differences
	TSS	TCu	DCu	TZn	DZn	
GBC	1.11	1.86	4.22	1.54	2.19	Okeover coefficients are derived from an asphalt road with limited heavy vehicles. The GoBus site is much coarser chipseal surface, with constant bus traffic manoeuvring over it, and therefore higher sediment and metal concentrations are expected.
GBD	6.54	0.82	0.33	13.94	19.97	The high TSS coefficient is likely to be due to the Okeover galvanised roof having very low TSS loads. The zinc concentrations from this old roof were substantially higher than any observed from the Okeover galvanised roof, likely due to the older age and weathering of the GoBus roof. Lower copper concentrations were observed, but neither the Okeover nor Addington galvanised roofs had particularly high copper concentrations.
KRC	1.60	0.85	0.94	3.71	3.34	The presence of heavy vehicles at the Kiwirail site may account for the higher sediment and zinc (tyre rubber-sourced) concentrations. Total copper is relatively similar, but the reduced amount may be a result of less stop-start traffic movements and therefore less brake use (copper sourced from brake pad wear).
LNR	0.77	1.46	2.10	3.09	5.06	While Lincoln Road has a higher annual average daily traffic (AADT) volume than the Okeover sampled road, the lower TSS may result from more frequent street sweeping[1]. While copper is similar, zinc is higher and may reflect the increased volume of tyre wear.
PCR	1.36	1.28	1.87	5.34	8.50	As for Lincoln Road, more frequent street sweeping[1] may be the cause of the lower TSS. An increased volume of tyre wear may be causing the higher zinc.
TJC	0.86	0.81	1.54	1.54	1.85	Carpark maintenance (sweeping) may contribute to a lower sediment concentration. Total copper is relatively similar.
TJD	5.81	2.71	1.10	2.54	3.45	The high TSS coefficient is likely to be due to the Okeover galvanised roof having very low TSS loads. The unpainted Addington roof leaches higher concentrations of zinc than the painted Okeover roof, despite the Okeover roof being much older. Much more of the zinc was in dissolved form, consistent with the higher ratio of dissolved metals seen in the Addington samples than the Okeover samples.

[1] Both Lincoln Road and Blenheim Road are scheduled for fortnightly street sweeping. High profile arterials (e.g. shops, malls) are swept fortnightly; other arterials and some collectors are 4 weekly; locals are either 6 or 8 weekly (M. Pinney (CCC), personal communication, 25 February 2016).

Table 7-9: Calibration Method 3 – Optimised MEDUSA model coefficient values for Addington catchment

Surface[1]	TSS Coefficients (Chapter 6: Eqns. 6-4 and 6-6)		
	a_1	a_2	k
Galvanised roof moderate (TJD)	2.38	0.46	9.33×10^{-3}
Galvanised roof old (GBD)	1.82	0.50	9.33×10^{-3}
Major arterial road (PCR)	282	0.34	9.33×10^{-3}
Minor arterial road (LNR)	216	0.17	8.0×10^{-4}
Commercial carpark (TJC)	190	0.28	8.0×10^{-4}
Industrial carpark standard (KRC)	396	0.21	8.0×10^{-4}
Industrial carpark manoeuvring (GBC)	319	0.19	8.0×10^{-4}

Surface	TCu Coefficients (Eqns. 6-14 to 6-17, 6-22)										
	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	Z	g_1	i_1
Galvanised roof moderate (TJD)	2	-2	0.4	0.37	2.8	-0.09	13.5	-3.732	0.75		
Galvanised roof old (GBD)	0.8	-2.8	0.55	1	2.1	-0.0001	4.6	-3.732	0.75		
Major arterial road (PCR)										0.440	
Minor arterial road (LNR)										0.810	
Commercial carpark (TJC)											0.458
Industrial carpark standard (KRC)											0.254
Industrial carpark manoeuvring (GBC)											0.615

Surface	TZn Coefficients (Eqns. 6-18 to 6-21, 6-23)										
	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	Z	h_1	j_1
Galvanised roof moderate (TJD)	22	4	0.2	0.09	0.64	-2	-0.17	2.122	0.75		
Galvanised roof old (GBD)	625	2	0.14	0.11	0.61	-2	-0.03	3.2	0.75		
Major arterial road (PCR)										7.990	

Surface	**TZn Coefficients (Eqns. 6-18 to 6-21, 6-23)**										
	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	Z	h_1	j_1
Minor arterial road (LNR)										7.250	
Commercial carpark (TJC)											3.750
Industrial carpark standard (KRC)											4.450
Industrial carpark manoeuvring (GBC)											2.50

Surface	**DCu Coefficients (Chapter 6: Eqn. 6-26)**
	l_1
Galvanised roof moderate (TJD)	0.23
Galvanised roof old (GBD)	0.20
Major arterial road (PCR)	0.33
Minor arterial road (LNR)	0.38
Commercial carpark (TJC)	0.46
Industrial carpark standard (KRC)	0.22
Industrial carpark manoeuvring (GBC)	0.52

Surface	**DZn Coefficients (Chapter 6: Eqn. 6-27)**
	m_1
Galvanised roof moderate (TJD)	1.00
Galvanised roof old (GBD)	0.85
Major arterial road (PCR)	0.59
Minor arterial road (LNR)	0.64
Commercial carpark (TJC)	0.52
Industrial carpark standard (KRC)	0.29
Industrial carpark manoeuvring (GBC)	0.56

Table 7-10: Comparison of model goodness of fit statistics between Calibration Methods 1 to 3 for each sampled surface

Surface	NSE			PBIAS		
	Okeover-calibrated coefficient values	Okeover-calibrated with scalar multipliers	Addington-calibrated coefficient values	Okeover-calibrated coefficient values	Okeover-calibrated with scalar multipliers	Addington-calibrated coefficient values
	Method 1	Method 2	Method 3	Method 1	Method 2	Method 3
TSS						
GBC	0.97	0.98	0.98	-1.6	-1.1	-1.0
GBD	-0.97	0.40	0.48	-30.6	-32.6	-18.9
KRC	0.78	0.81	0.83	-4.9	-3.3	-3.0
LNR	0.85	0.93	0.94	5.2	2.5	2.6
PCR	0.74	0.71	0.76	0.5	0.2	0.2
TJC	0.73	0.77	0.80	7.7	3.6	3.7
TJD	-1.19	0.96	0.97	-34.6	-22.5	-13.3
Total copper						
GBC	-1.69	-0.80	-0.65	-7.9	-5.7	-5.0
GBD	0.65	0.73	0.81	9.5	6.0	6.4
KRC	0.86	0.91	0.89	4.0	2.5	2.6
LNR	0.81	0.90	0.91	-6.0	-3.3	-3.0
PCR	0.87	0.92	0.94	-4.0	-2.2	-2.0
TJC	0.91	0.97	0.96	4.5	2.2	2.3
TJD	0.45	0.61	0.66	-14.3	-6.8	-5.2
Dissolved copper						
GBC	-16.18	-6.93	-5.66	-21.0	-18.9	-13.0
GBD	-1.09	0.73	0.71	59.4	27.2	49.5
KRC	-1.17	-1.06	-0.82	12.5	7.9	8.1
LNR	0.03	0.38	0.43	-12.2	-7.6	-6.1
PCR	-2.58	-2.00	-1.95	-9.4	-5.6	-4.7
TJC	-0.99	-0.68	-0.73	-6.9	-4.0	-3.5
TJD	0.89	0.89	0.90	-0.3	-0.1	-0.1
Total zinc						
GBC	0.39	0.69	0.70	-5.2	-3.5	-3.3
GBD	-8.39	0.85	0.81	-24.0	-21.3	-15.3
KRC	-0.01	0.86	0.86	-15.0	-11.3	-9.2
LNR	-3.44	0.28	0.30	-13.5	-7.7	-6.5
PCR	-4.46	0.85	0.80	-19.9	-12.3	-9.6
TJC	0.83	0.93	0.94	-5.5	-2.9	-2.7
TJD	0.46	0.99	0.87	-10.3	-4.6	-4.0
Dissolved zinc						
GBC	-0.85	0.09	0.13	-9.6	-6.9	-6.0
GBD	-11.45	0.74	0.80	-27.3	-25.5	-17.4

Surface	NSE			PBIAS		
	Okeover-calibrated coefficient values	**Okeover-calibrated with scalar multipliers**	**Addington-calibrated coefficient values**	**Okeover-calibrated coefficient values**	**Okeover-calibrated with scalar multipliers**	**Addington-calibrated coefficient values**
	Method 1	**Method 2**	**Method 3**	**Method 1**	**Method 2**	**Method 3**
KRC	-0.06	0.26	0.34	-11.8	-8.7	-7.1
LNR	-7.16	-0.60	-0.50	-20.0	-12.6	-9.6
PCR	-28.42	-1.74	-2.03	-25.3	-17.1	-12.0
TJC	0.25	0.90	0.86	-9.2	-5.2	-4.6
TJD	-0.03	0.99	0.89	-13.9	-6.5	-5.4

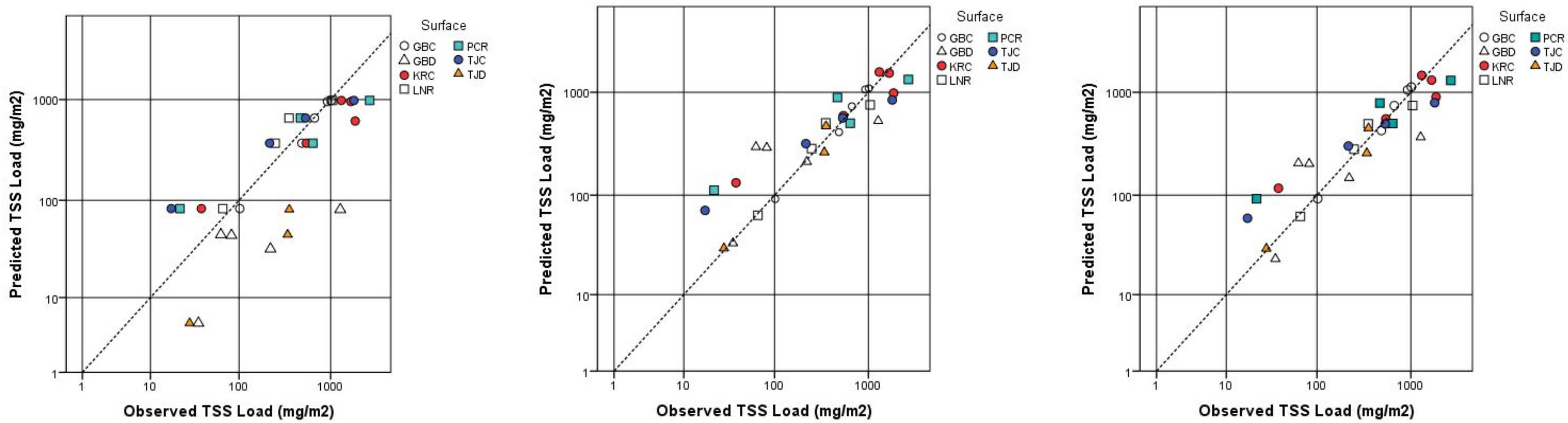


Figure 7-7: Observed TSS loads against MEDUSA predicted loads using Calibration Methods 1 to 3 (from left to right)

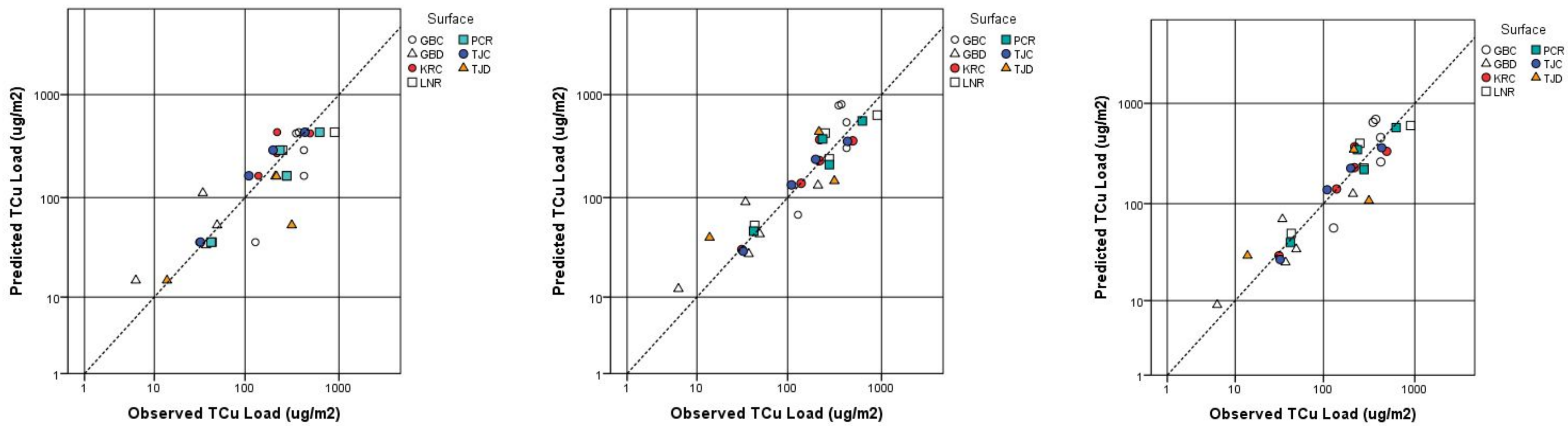


Figure 7-8: Observed total copper loads against MEDUSA predicted loads using Calibration Methods 1 to 3 (from left to right)

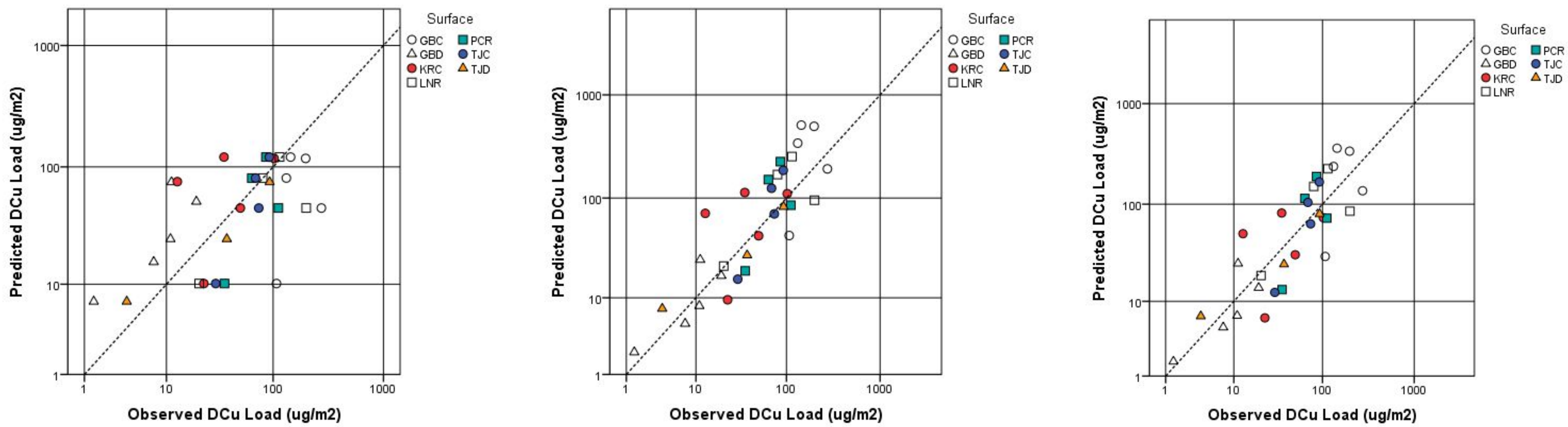


Figure 7-9: Observed dissolved copper loads against MEDUSA predicted loads using Calibration Methods 1 to 3 (from left to right)

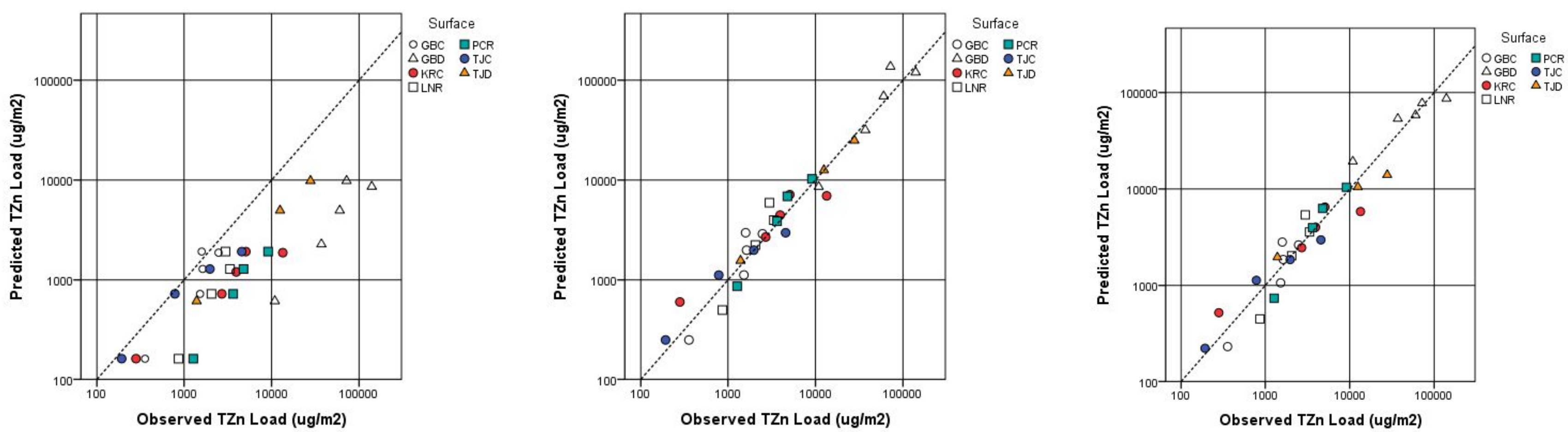


Figure 7-10: Observed total zinc loads against MEDUSA predicted loads using Calibration Methods 1 to 3 (from left to right)

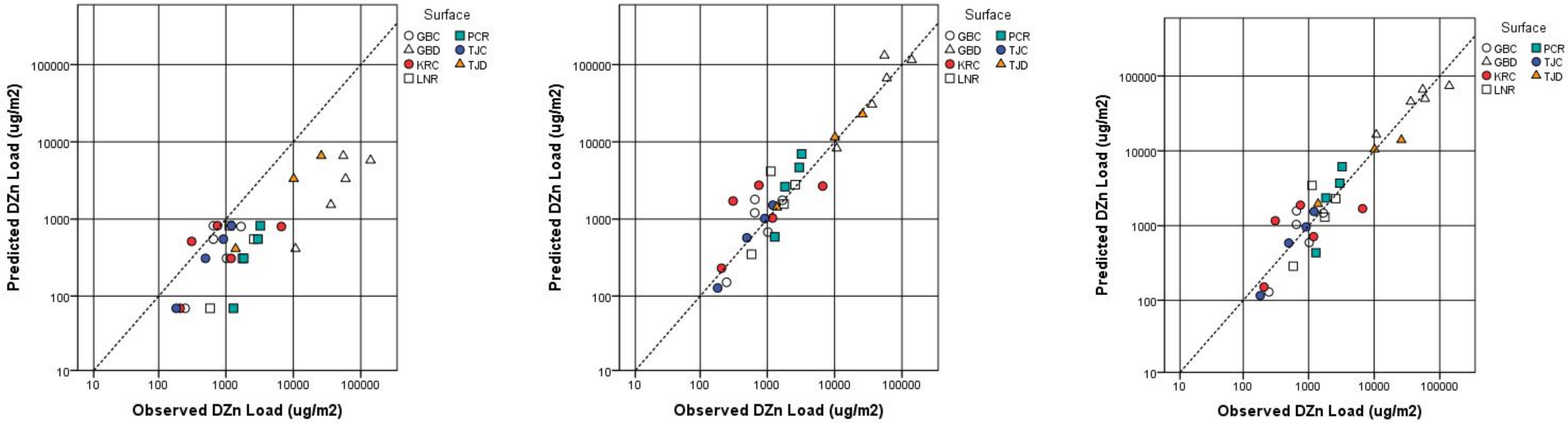


Figure 7-11: Observed dissolved zinc loads against MEDUSA predicted loads using Calibration Methods 1 to 3 (from left to right)

7.5.1 Calibrated model simulation results

MEDUSA was run for the Addington catchment for a full year of rain events from the year 2012 (refer to Appendix G for rainfall event characteristics), using the recalibrated model coefficient values (Calibration Method 3).

Relative contribution of pollutant by surface type

The pollutant load per area (mg/m^2 or µg/m^2) was derived for each roof, road and carpark subcategory and mapped across the Addington catchment (Figure 7-12 to Figure 7-14). The loads (per area) indicate *which types* of surfaces are of most concern in terms of their relative contribution of pollutants, independent of the surface area.

TSS loads (per area) were highest from collector and local roads, while major and minor arterial roads were found to have lower TSS levels, likely due to street sweeping, in line with carpark TSS levels. TSS levels from all roof types were lower than any road or carpark type.

Total copper loads (per area) were highest from industrial carparks that have been classified as having heavy vehicles manoeuvring across them. These are followed, in order of decreasing loads (per area), by major arterial roads, minor arterial roads, remaining road types, then commercial and standard industrial carparks. Again, all roof types produce considerably lower total copper loads than any road or carpark surface.

Conversely, the highest total zinc loads (per area) were from old galvanised roofs, followed by moderate and new galvanised roofs. These galvanised roofs all produce substantially more total zinc loads (per area) than any of the other surface types in the catchment.

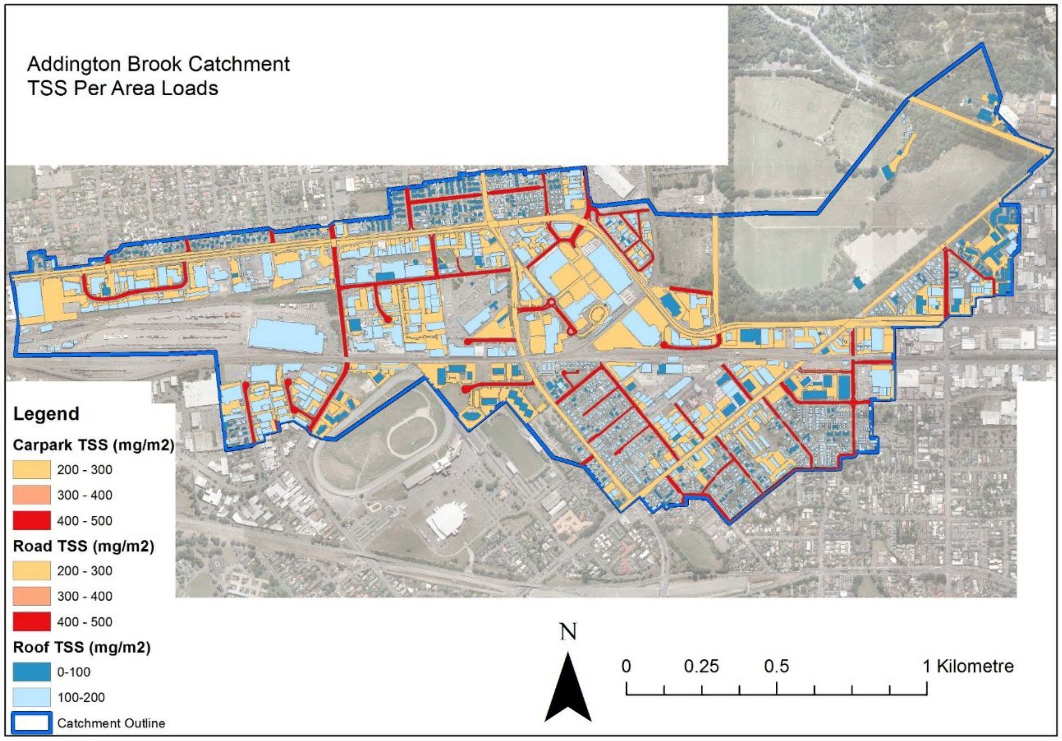


Figure 7-12: TSS per area loads (mg/m^2) derived from 2012 rainfall events

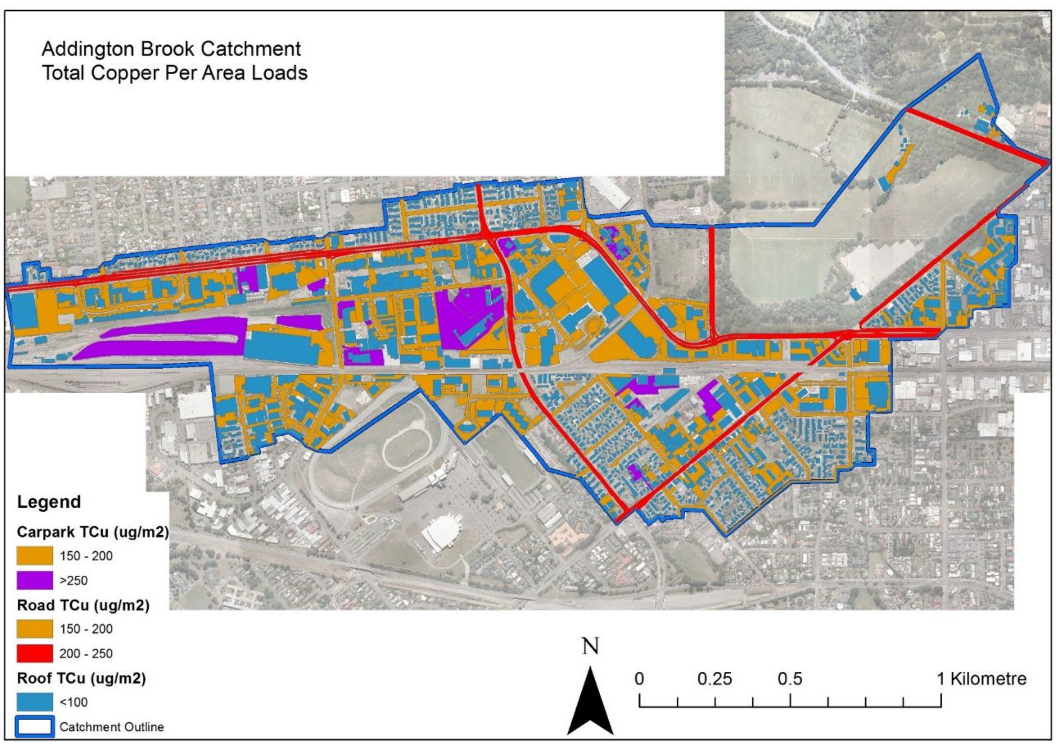


Figure 7-13: Total copper per area loads (µg/m^2) derived from 2012 rainfall events

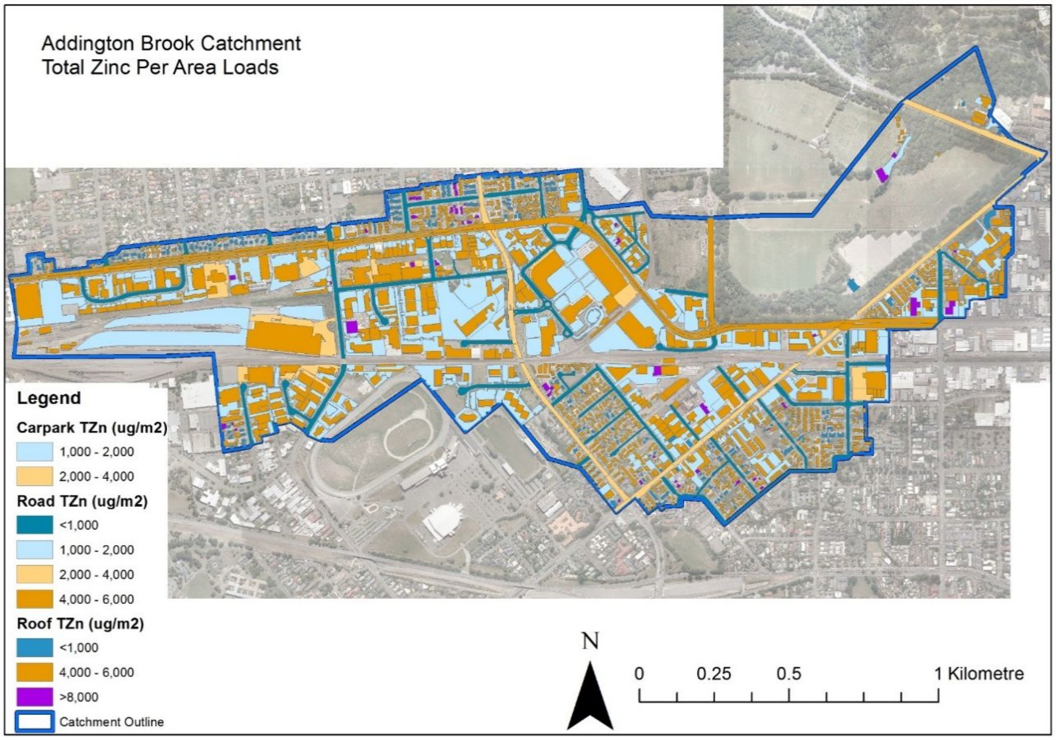


Figure 7-14: Total zinc per area loads (μg/m^2) derived from 2012 rainfall events

Average event load

The average event loads for the catchment were derived from the 88 modelled rain events of 2012 and mapped across the Addington catchment (Figure 7-15 to Figure 7-17). The average event load maps show how much pollutant is predicted to be contributed by *each individual surface* once the surface material and the total surface area is taken into account. Accordingly, only carpark and roof surfaces were mapped as their area is associated directly with individual properties. Roads, by contrast, are linear features and per area loads are a more relevant way to visually show their contribution of pollutants.

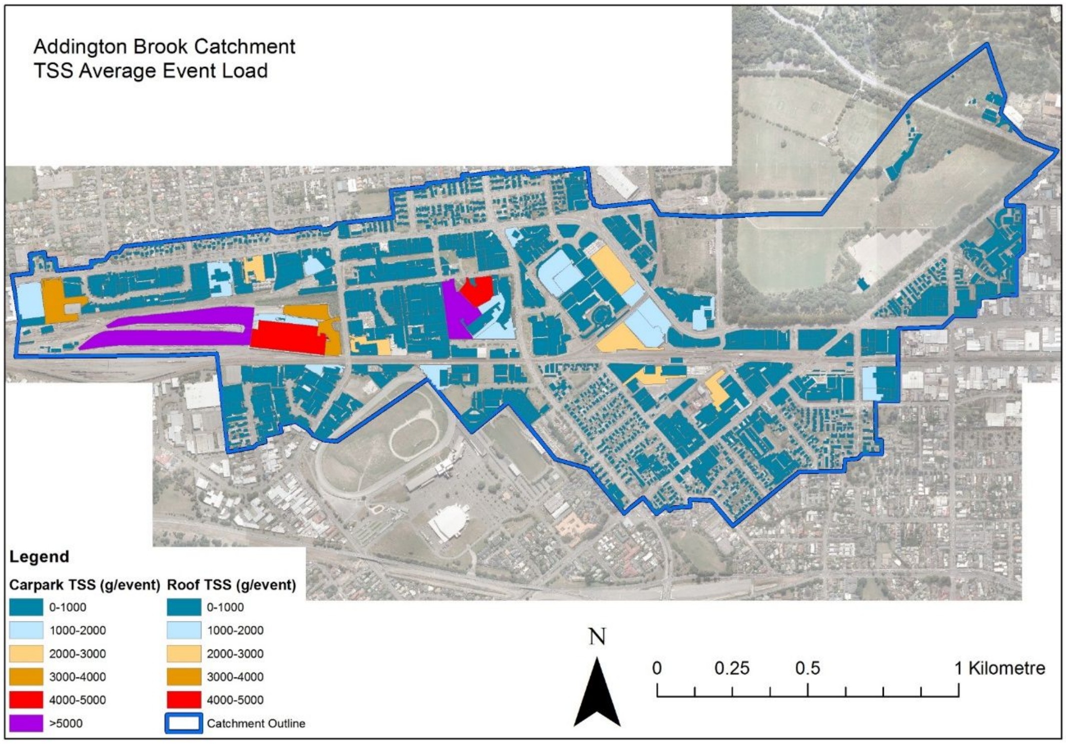


Figure 7-15: TSS average event loads (g/event) derived from 2012 rainfall events

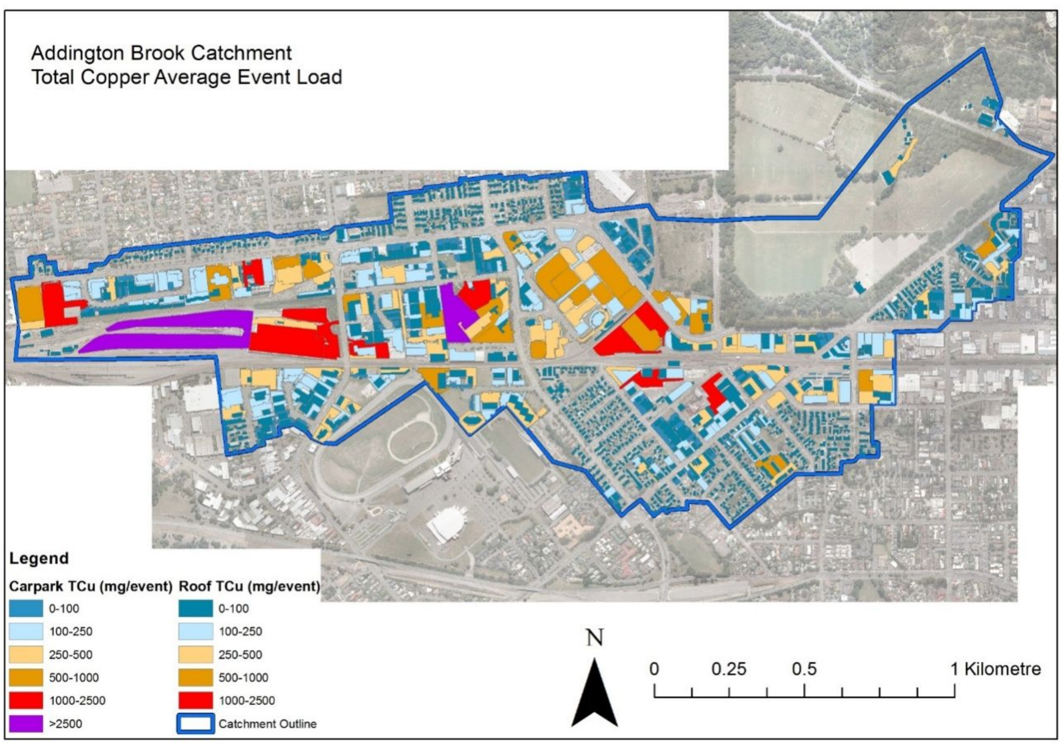


Figure 7-16: Total copper average event loads (mg/event) derived from 2012 rainfall events

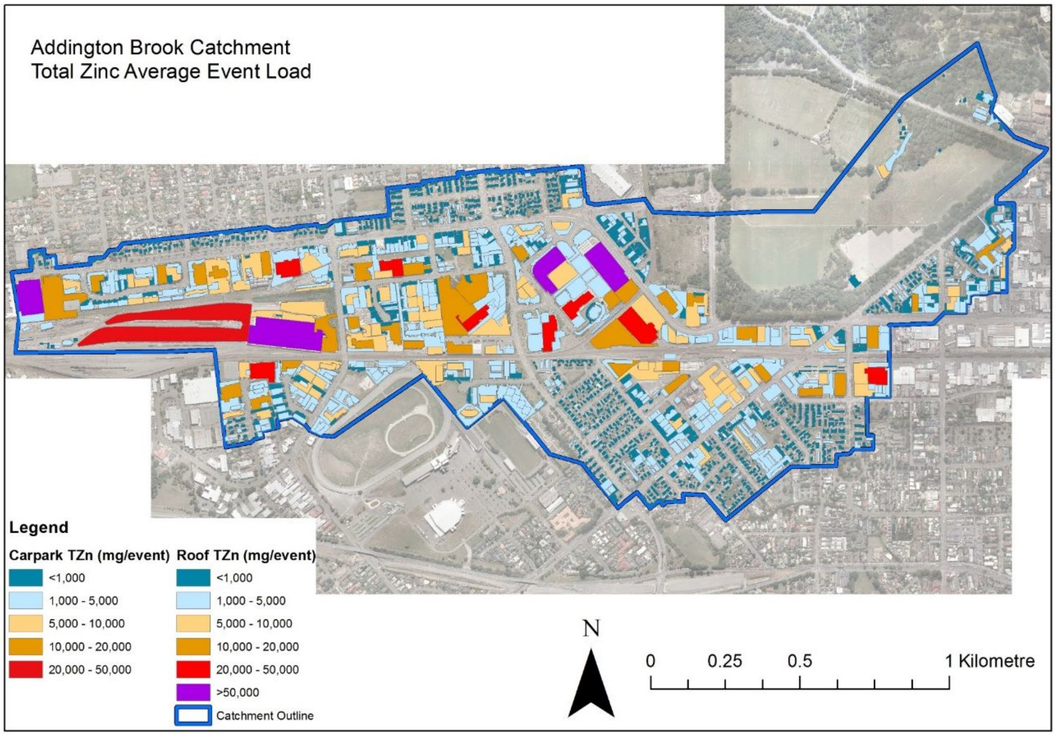


Figure 7-17: Total zinc average event loads (mg/event) derived from 2012 rainfall events

A comparison of average event loads from each main surface type against the relative surface areas of each type clearly shows how road and carpark surfaces contribute a greater proportion of TSS and total copper than their relative area, while roofs (primarily galvanised) contribute substantially more total zinc than their relative area (Figure 7-18).

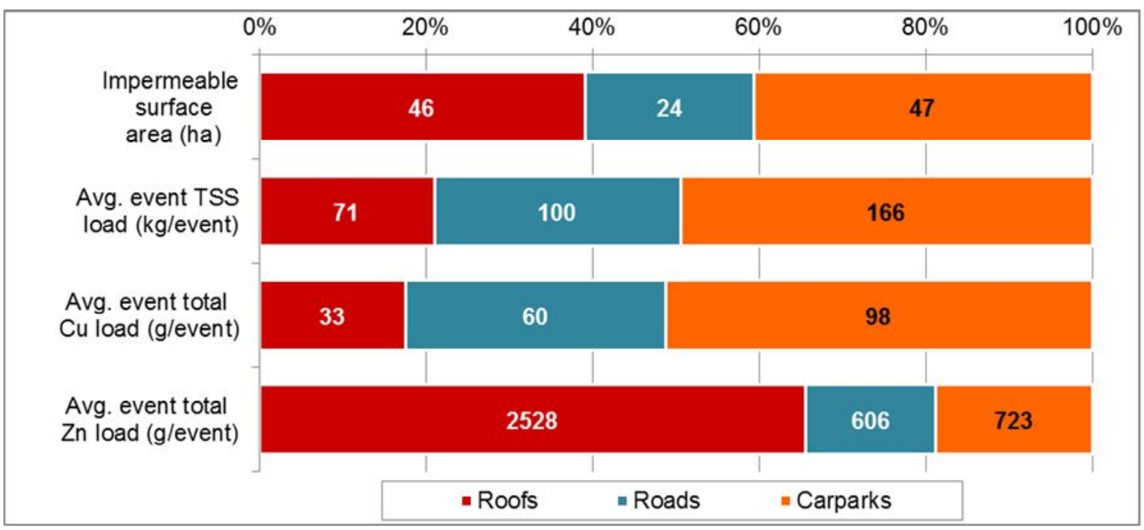


Figure 7-18: Average event loads from 2012 rainfall events compared to the relative areas of roofs, roads and carparks in Addington catchment

Annual loads

Annual loads were calculated by summing the predicted loads from all 88 rain events in 2012 (Table 7-11). From a quantity perspective, sediment is the major pollutant, with over 30 tonnes predicted to be generated in the catchment over a typical year. Zinc is the next largest pollutant load, with 341 kg predicted over a year period, of which 59% is predicted to be released by galvanised roofs. The annual copper load is predicted to be 17 kg, with 82% of the copper contributed by road and carpark runoff.

Table 7-11: Annual pollutant loads by surface type for the 2012 year

Surface Type	Subcategory	TSS (kg/yr)	TCu (kg/yr)	TZn (kg/yr)
Roof	Butynol All	1	0.004	0.009
	Concrete All	35	0.13	0.28
	Decramastic All	8	0.03	0.06
	Fibreglass All	1	0.003	0.006
	Galvanised New	444	0.18	13.8
	Galvanised Moderate	6,450	2.6	200.9
	Galvanised Old	104	0.07	9.4
	SUBTOTAL	*7,043*	*3.0*	*224.5*
Road	Private	16	0.007	0.03
	Local Road	4,138	1.8	8.1
	Collector	753	0.33	1.5
	Minor arterial	1,665	1.3	11.6
	Major arterial	2,181	1.7	32.1
	SUBTOTAL	*8,753*	*5.1*	*53.3*
Carpark	Commercial	6,893	4.9	38.9
	Industrial Manoeuvring	5,601	3.0	13.6
	Industrial Standard	2,101	0.66	11.1
	SUBTOTAL	*14,595*	*8.6*	*63.6*
TOTAL		**30,392**	**16.8**	**341.3**

Distribution of modelled event loads

Maximum loads were predicted to have occurred for the same event, SF54 on 12 August 2012, for TSS, total copper and total zinc. This is likely due to the long duration of the event (41 hours). While this event produced the maximum loads from all surface types, it was also the maximum-load-producing event for roof, road and carpark surfaces individually. This single event contributed 10.6% of the annual TSS load, 10.9% of the annual total copper load and 11.2% of the annual total zinc load. Minimum loads were also predicted to have occurred for all three pollutants on the same event, SF40 on 14 June 2012, which had a short antecedent dry period which would have limited dry weather pollutant build-up.

The distribution of event loads was markedly left-skewed for all pollutant types and surfaces, indicating that a substantial proportion of the load is being contributing by a small number of high load-producing events (Figure 7-19).

The seasonal distribution of generated loads was similar for each pollutant, with the highest load being generated in winter (contributing over 40% of the annual TSS, total copper and total zinc loads) (Table 7-12).

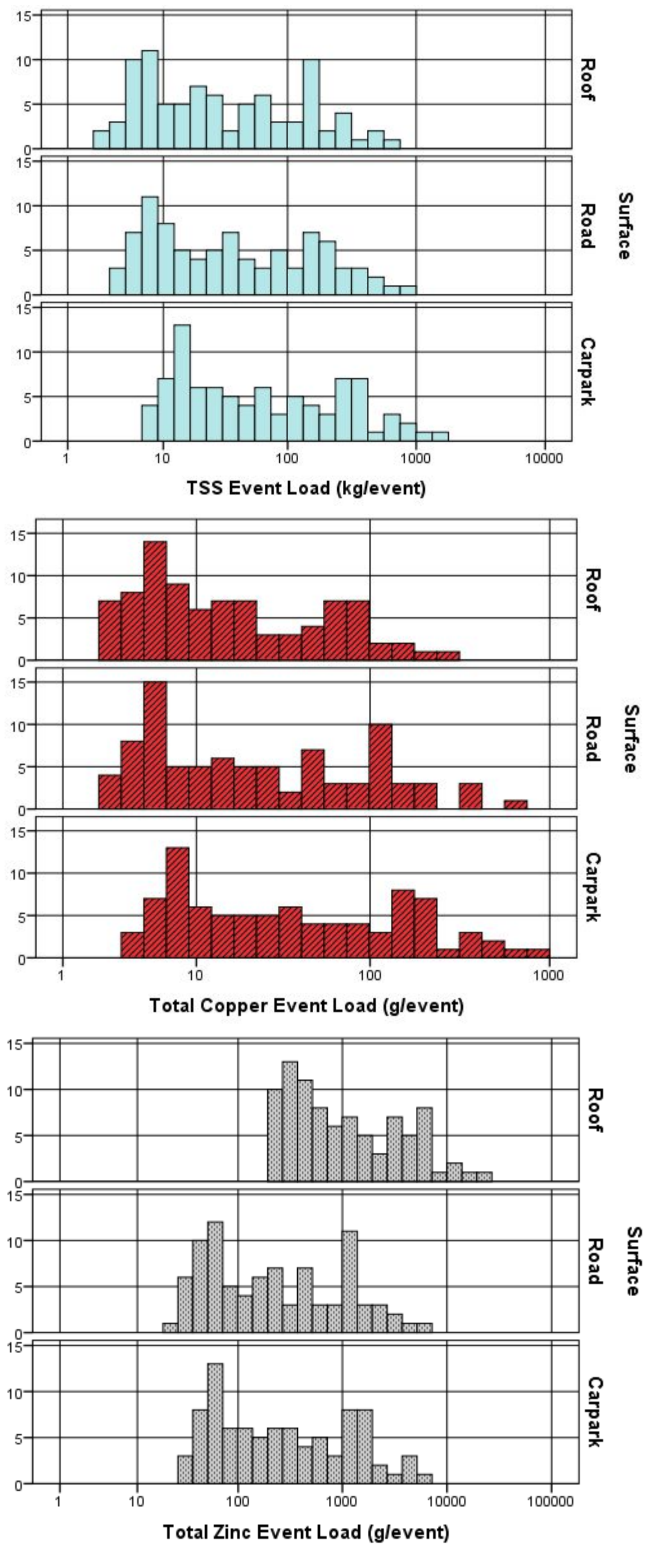


Figure 7-19: Frequency distribution of event loads from 2012 rainfall event by surface type

Table 7-12: Seasonal contribution of pollutant loads in 2012

Season	No. of rain events	TSS load	Total copper load	Total zinc load
		As a percentage of annual load		
Summer	22	17%	17%	17%
Autumn	18	19%	18%	17%
Winter	25	41%	42%	44%
Spring	23	23%	23%	22%

Load variation in response to rainfall characteristics

MEDUSA was run for seven ‘representative’ rainfall events (Table 7-13). Event 1 was derived from the median values from the 2012 rain events. The remaining six events explore the low and high ends that could be expected for ADD, average intensity and duration in a typical year, by changing one rainfall variable value away while holding the other variables at their median values. This enables sensitivity testing of the event loads’ response to variation in one rainfall variable. While the representative events may not necessarily match exact events from the year 2012, the low and high bounds for each rainfall characteristics are within the range of values observed each characteristic over the 88 events of the year 2012. The difference between the low and high value for each parameter is a factor of 20. As rainfall pH was not found to significantly vary, it has been held constant for the representative rainfall events at a mean value of 6.01. It should be noted that extreme events are intentionally not represented in these scenarios, as the model is focused on predicting pollutant loads from typical rain events and the calibration data from both the Okeover and Addington catchments does not include any extreme events.

Table 7-13: Representative rainfall scenarios

Rainfall parameter	Event 1	Event 2	Event 3	Event 4	Event 5	Event 6	Event 7
	Median	Low ADD	High ADD	Low intensity	High intensity	Short duration	Long duration
Rainfall pH	*6.01*	6.01	6.01	6.01	6.01	6.01	6.01
ADD (days)	*3*	*1*	*20*	3	3	3	3
Average intensity (mm/hr)	*0.53*	0.53	0.53	*0.20*	*4.00*	0.53	0.53
Duration (hrs)	*5*	5	5	5	5	*1*	*20*

TSS loads were found to be most sensitive to increases in average rainfall intensity of the four parameters used in the model, followed by the duration of rain event (Figure 7-20). Total copper and zinc loads showed a similar response. The results are presented as a ratio of the predicted scenario load to the ‘basecase’ load predicted when all the rainfall variables are median values (i.e. Event 1).

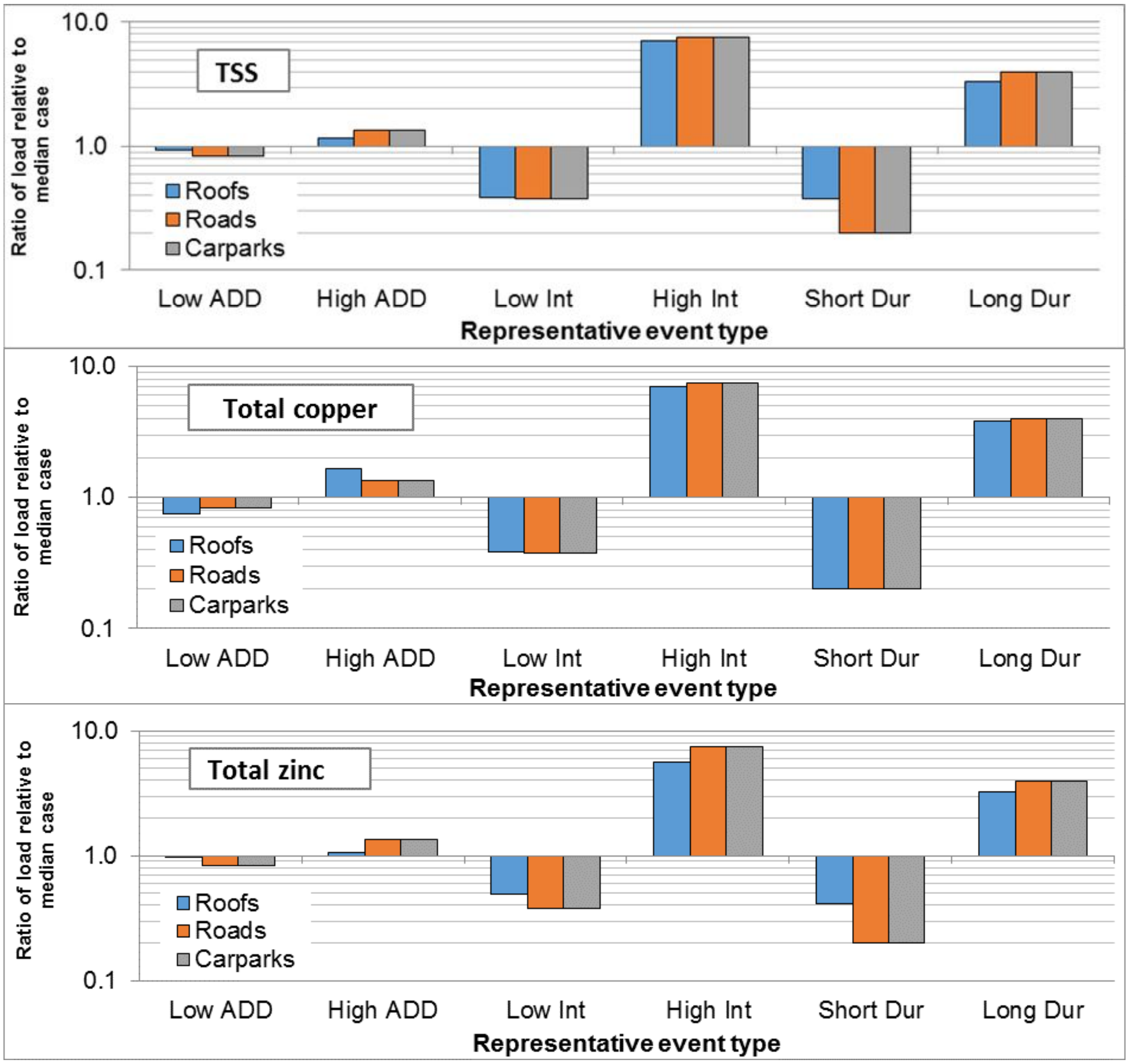


Figure 7-20: Ratio of event loads for representative rainfall events relative to median (Event 1; refer to Table 7-13)

7.6 Discussion

7.6.1 Pollutant sources

The range of pollutant concentrations seen in the Addington runoff were consistently higher than those seen in the Okeover surfaces of similar type (Table 7-7). Possible reasons for the differences observed between the two catchments include: variance in the age, orientation and condition of the roofs, variance in age and condition of the asphalt sealing of the road surfaces, and variance in the contribution of atmospheric deposition to the pollutant load available on the surfaces. The Addington catchment is also closer to the Port Hills than the Okeover catchment (2.5 km distance compared to 5.6 km at their closest points, respectively). The loess soils of the Port Hills have been identified as a likely cause of proportionally higher levels of atmospherically-deposited particles in relation to an area's proximity to the hills (Murphy *et al.* 2014).

The higher amount of TSS in carpark runoff compared to road runoff confirms the importance of characterising carpark surfaces separately from road surfaces for pollutant load modelling, despite the pollutant sources being the same. The differences are likely to be due to factors such as maintenance such as street sweeping removing road-deposited sediment, as well as increased rate of sediment deposition from manoeuvring vehicles at the carpark sites.

7.6.2 Effectiveness of model calibration and suitability of model

The modelled load correlations from Calibration Method 1 were generally high (for example, the model predicted low loads for event where low loads were observed, and predicted high loads for high observed load events), however the overall model fit was poor and a scalar multiplier (i.e. Calibration Method 2) significantly improved the model predictive performance, particularly for total zinc (and for dissolved copper and zinc).

The good performance of the Calibration Method 2 version of the model (particularly in comparison to the full calibration of model coefficients undertaken in Calibration Method 3) demonstrates that the use of a scalar multiplier is a reasonable, efficient approach to calibrate this model for surfaces in other catchments that share similar characteristics and environmental conditions to the Okeover sampled surfaces. The NSE values for Calibration Method 2 are not substantially different than what could be achieved for Calibration Method 3 (Table 7-10). However, this could not be expected if the model was applied to a catchment in a different geographic region. Under such conditions, a recalibration of the model coefficient values for each sampled surface (i.e. the Calibration Method 3 process) would be needed.

7.6.3 Pollutant processes in the Addington catchment

The model was effective at predicting pollutant loads over a wide range of loads (i.e. variations of several orders of magnitude), and produced moderate to strong NSEs for TSS, total copper and total zinc predictions for all sampled surfaces, with the sole exception of the industrial manoeuvring carpark site. The calibration results suggests that the processes for pollutant build-up and wash-off as expressed in the MEDUSA model equations are similar between the Okeover and Addington, but that the magnitude of pollutants available is greater in Addington (i.e. the rate of pollutant build-up is higher). Appendix I provides a comparative summary of the calibrated model coefficient values for all sampled surfaces across both the Okeover and Addington catchments.

The poor model performance for the total copper load predictions from the industrial manoeuvring carpark site are likely due to the model framework not adequately representing the process of direct deposition of copper from brake pad wear from manoeuvring heavy vehicles at the site, as the model currently assumes copper to be proportional to TSS for such carpark surfaces. This site had the highest average total copper concentrations of the seven sampled sites, likely due to the contribution from heavy vehicles. As sediment from brake pad wear is known to be very fine (Garg *et al.* 2000; Zanders

2005), it therefore contributes proportionately little mass to the overall TSS concentration and the relationship of copper concentration to TSS cannot be expected to be consistent between events at such a site.

7.6.4 Influence of rainfall characteristics on pollutant generation

The modelling showed that pollutant generation was most sensitive to variation in rainfall intensity and duration. This suggests that the rate of pollutant generation in the system is more dependent on what is stored long-term in the system (and is only dislodged by higher intensity or longer duration events), than the amount of pollutant that is accumulated during the immediate antecedent dry period. Furthermore, regardless of the elevated concentrations seen in the first flush samples, a substantial portion of the annual load comes from the longer duration events where the first flush is only a minor portion of the event runoff volume. Therefore, a focus on first flush treatment may have limited benefits for reducing pollutant loads on an annual timescale.

Both the intensity and duration of rain events are expected to change under projected climate change scenarios for Christchurch (Christchurch City Council 2002; NIWA 2011). The model could be used to simulate potential climatic change scenarios to help understand future trends of pollution loadings of our urban streams.

7.7 Conclusions

The application of MEDUSA to the Addington Brook catchment demonstrated how an optimised sampling and calibration process could be used to efficiently reapply MEDUSA to a new catchment. Three calibration method were trialled, and a simpler method based on using a scalar multiplier to adjust Okeover-calibrated model loads to Addington observed loads was found to perform similarly well to a full recalibration of the model coefficient values. The process was also successful at characterising and modelling seven new surface types that had not previously been characterised in the Okeover catchment.

The model was effective at predicting pollutant loads over a wide range of loads (i.e. variations of several orders of magnitude), and produced moderate to strong NSEs for TSS, total copper and total zinc predictions for all sampled surfaces, with the sole exception of the industrial manoeuvring carpark site. It was only effective at predicting dissolved copper loads from three of the seven sampled surfaces types, but was effective at predicting dissolved zinc loads at five of the seven sites.

When the calibrated MEDUSA model is run for the Addington catchment, it predicts that TSS is the major pollutant with the majority of the sediment being contributed from carpark runoff, followed by road runoff. Except where roof areas are very large, roof surfaces are not a significant contributor to TSS loads in the catchment.

Zinc is next highest pollutant load entering the brook. The most significant contributors of zinc are galvanised roofs in the catchment, in particular old, weathered galvanised roofs (the total zinc loads per area from these old galvanised roofs are substantially higher than any other surface type). Zinc discharges from these roofs are primarily in dissolved form (upwards of 89% dissolved), while between 35-55% of zinc from roads and carparks is in dissolved form. These findings indicate that the implementation of source reduction policies such as replacement of old metal roofs or a requirement to treat runoff onsite from large galvanised roofs (using a treatment process that is effective for dissolved metals) would be appropriate to reduce total zinc loads in the catchment.

Copper is primarily contributed from roads (in particular, major arterial roads) and industrial carparks (in particular, where heavy vehicles are manoeuvring at the site). 25-47% of the copper from roads and carparks is in dissolved form. All first flush and the majority of steady state samples from the road and carpark sampling sites were above the *instream* guideline values (some by an order of magnitude or more), and therefore treatment, dilution and/or mixing would be required for the runoff concentrations to meet to the *instream* guideline values.

These findings provide a sound basis for the prioritisation of surfaces or properties to target for improved stormwater management.

8 Conclusions and Research Recommendations

8.1 Overview

This research had four key components:

1. Characterisation of untreated runoff quality (TSS and heavy metals) from different urban surfaces;
2. Characterisation of the variation in particle distribution of the TSS in the runoff and its implication on treatment selection and performance;
3. Development of an event-based pollutant load model that uses rainfall characteristics to predict the amount of TSS, total and dissolved copper and zinc from individual impermeable surfaces in a catchment; and
4. Calibration and application of the model in two case study catchments to assess model performance and its ability to be recalibrated for different catchments.

An extensive dataset of runoff quality was developed from untreated runoff sampling of a road, galvanised roof, copper roof and concrete roof over a 15-month period. This dataset was used for the characterisation studies and then was also used to calibrate the new model. A second sampling programme was also undertaken to recalibrate the model for the second catchment. The model framework was developed using numerical modelling and GIS analysis.

This research has therefore contributed to the scientific understanding of:

- The relationships between different urban surface types and pollutant generation, (i.e. the relative influence of rainfall and material characteristics in generation of both sediment and metal pollutants);
- Partitioning of heavy metals in untreated runoff between particulate and dissolved state from different urban surfaces;
- Variance in PSD during and between rain events, and the implications of that variance on treatment performance;
- The importance of using a disaggregated model (i.e. individual surface-based modelling) as the pollutant generation processes differ significantly between different urban surface types

8.2 Conclusions

8.2.1 Total suspended solids

Of all the impervious surfaces monitored in this research, roads and carparks were the primary contributors of sediment to urban runoff and should be targeted for total suspended solids (TSS) removal. Furthermore, the substantial difference between road and roof TSS concentrations indicate that treatment of road runoff prior to it mixing with other runoff (e.g. from roof surfaces, in the kerb and channel) may be warranted to limit the ‘treatable’ volume and minimise the required capacity of any treatment system.

The copper roof runoff had consistently high first flush TSS concentrations, thought to result from copper patination of the (old) roof material during dry weather rather than atmospheric dust retention. However, steady state TSS concentrations in the copper roof runoff were very low, indicating that this patination byproduct was readily washed off in the initial stages of each rain event, and overall would contribute only a limited amount to the total sediment load produced in a catchment. The low TSS in both galvanised and concrete roof runoff suggest individual treatment of these surface types for TSS is not required.

TSS had a significant first flush effect. However, MEDUSA predicted that for the Addington catchment throughout 2012, TSS concentrations were most sensitive to rainfall intensity and duration. Furthermore, regardless of the elevated concentrations from the first flush, a substantial portion of the annual TSS load comes from the longer duration events where the first flush is only a minor portion of the event runoff volume (e.g. one 41 hour long rain event was predicted to have contributed over 10% of the annual TSS load). Therefore, a focus on capturing and removing sediment within the first flush period alone may have limited benefits for reducing pollutant loads on an annual timescale.

8.2.2 Particle size distribution

The similar particle size distributions (PSDs) of all four surfaces' runoff suggest that wind-blown loess soils circulating in Christchurch's airshed may be a specific contributor to sediment on urban surfaces, and leads to a more centralised PSD profile than what has been reported elsewhere. In particular, the representative PSD profile developed by the National Urban Runoff Program (NURP) in the US (Driscoll 1986) and used widely as an assumed PSD for urban runoff, is considerably finer than any of the four surfaces sampled in this study, highlighting the importance of characterising sediment in local runoff for optimal selection of a sediment removal system.

Intra-event PSD variation was generally not significant, but substantial inter-event variation was observed, particularly for coarser road and concrete roof surfaces. The wide range in PSD from this study's surfaces, particularly the road surface with its high overall TSS, suggests short-retention treatment devices carry a high performance risk of not being able to achieve adequate TSS removal across all rain events. While treatment systems with significant retention times such as wetlands enables settling of the finer sediments, these are typically only feasible for centralised systems where runoff is collected from a larger catchment area. Source reduction and on-site treatment approaches may be desirable to minimise or treat other pollutants conveyed in the runoff.

8.2.3 Heavy metals

At a mean concentration of 1,663 μg/L, copper roof runoff produced total copper concentrations over 50 times higher than the next highest copper contributing surface, the asphalt road (mean of 29 μg/L). While some mixing and transformation of the copper can be expected as the runoff is conveyed through the stormwater network and is discharged into the receiving waterway, these copper concentrations are nonetheless well in excess of local (mixed) instream guideline values to prevent ecotoxicity. Furthermore, the majority of the copper in the copper roof runoff was in dissolved form (average of 77% dissolved), while only 28% of the road runoff copper was in dissolved form. As well as contributing to toxicity in the receiving environment, dissolved metals in stormwater runoff can be more difficult to treat as majority of the standard stormwater treatment systems are based on filtration or settling processes that primarily aim to remove sediment. As steady state concentrations of copper from the copper roof are very high, there will be limited benefits of focusing on first flush treatment. Therefore, existing copper roofs should therefore be targeted for either replacement or painting to minimise copper dissolution and patination, while new copper roofs should be avoided. Road runoff treatment systems should consider removal of both dissolved and particulate metals, as removal of particulate-associated metals via settling or filtration may not adequately reduce metals loads entering urban waterways.

The galvanised roof runoff produced the highest total zinc concentrations (mean of 397 µg/L) under both first flush and steady state conditions. Almost all the zinc (average of 99%) was in dissolved form. Road runoff produced the next highest zinc concentrations (mean of 122 µg/L), however, only an average of 43% of the zinc in road runoff was in dissolved form. Galvanised roofs should be targeted for source reduction of zinc via roof replacement or repainting. Road runoff should also be managed for zinc; as source reduction options are limited (zinc in road runoff is sourced from vehicle tyre wear), treatment systems need to consider removal of both particulate and dissolved forms of zinc.

Lead was confirmed to exist at relatively low concentrations in the runoff from all four sampled surfaces. Therefore, stormwater monitored throughout this research was not contributing much lead to the receiving waterway. Any existing elevated instream lead concentrations found in other studies would likely be the result of lead bound to accumulated sediment on the streambed. Lead was therefore not included in the current MEDUSA model framework as the model purpose is the prediction of pollutant loads from current impervious surfaces, rather than assessing the legacy of instream pollutant loads.

Elevated alkalinity was seen in both road and concrete roof runoff. While these concentrations are not a pollutant concern, alkalinity will affect the partitioning of heavy metals in the runoff. Where runoff from metallic roof surfaces (e.g. copper or zinc-based roofs) is mixed with road runoff, the proportion of metals in particulate form may increase due to elevated alkalinity in the combined runoff and therefore more of the metal load could be removed via settling or filtration treatment systems.

8.2.4 Development of modelling framework

As pollutant concentrations were found to be significantly different between surfaces, it is appropriate that predictive models such as MEDUSA take account of the different surface materials, instead of being aggregated into more generalised categories such as land use. This modelling approach provides opportunity for identifying and targeting individual surfaces contributing disproportionately high amounts of pollutants (e.g. copper roofs). While MEDUSA predicts pollutant loads on an event basis, multiple rain events can also be run in the model and summed to give seasonal and annual loads. Surface loads can also be aggregated by property or subcatchment. This flexibility ensures that stormwater management decision-makers have guidance for a wide range of stormwater improvement objectives from individual storm events and surface types to wider catchment and annual management approaches.

The build-up and wash-off process-based MEDUSA model was effective for predicting TSS, copper and zinc loads in a low intensity rainfall climate. While the linear regression (LR) model (developed from the same dataset that was used to calibrate MEDUSA) was more accurate at pollutant load prediction than MEDUSA for the particular training dataset, both models were effective at predicting pollutant loads. The MEDUSA framework provides substantial benefits over a catchment-specific model such as the LR model, as it simulates ‘universal’ pollutant build-up and wash-off processes, while accounting for the relationships between pollutant loadings and rainfall characteristics to be incorporated. This allows MEDUSA to be recalibrated and applied to catchments with different climatic conditions and so offers a wider application to other urban catchments. In particular, while the model framework has been initially calibrated and applied to a low intensity rainfall climate with little variance in rainfall pH, the model framework in intended to enable calibration and application of MEDUSA in a wider range of climates than the case study climate of Christchurch, New Zealand. Therefore both rainfall pH and intensity are included as predictor variables. The application of MEDUSA to the Addington catchment demonstrated that a limited untreated runoff programme was sufficient to enable recalibration of the model, with good predictions of pollutant loads.

8.2.5 Model limitations

MEDUSA only currently predicts the pollutant loads as they are generated at each surface discharge point, and therefore does not account for changes in pollutant load as the runoff is conveyed through the stormwater network and is discharged in the receiving waterway. The model is also currently restricted in the rainfall characteristics that each pollutant load is related to within the model framework, as defined by Christchurch’s low intensity climate. The calibrated TSS coefficient values suggests that the Okeover copper roof was substantially more influenced by the number of antecedent dry days (ADD) than the concrete and galvanised roofs (i.e. higher ADD coefficient values). However, it is likely that the high TSS loads from copper roofs are not due directly to ADD, but simply a means by which the model can reproduce high TSS loads, and the model could better predict TSS loads from copper roofs using a wider range of variables (e.g. corrosion-related variables). Similarly, both the calibrated MEDUSA and LR model results suggest that factors beyond rainfall characteristics are important drivers of TSS build-up and wash-off, and would need to be included in the model framework to enable improved TSS load predictions.

8.3 Recommendations for further research

8.3.1 Pollutant transformations and transport from source to receiving environment

Pollutant concentrations and metals partitioning will change as the runoff from an individual surface mixes with runoff from other surfaces, and is conveyed through the stormwater system and then mixes instream within the receiving waterway. Therefore, optimal at or near-source pollutant treatment systems may be different from optimal far-source (i.e. downstream) or mixed runoff treatment systems. Further research is needed to understand and predict how the pollutants will transform from source to receiving environment and the associated timing of pollutant transport. A longitudinal study of pollutant character from source to mixed instream is suggested to explore this.

In areas where groundwater is readily connected to surface waters (as in Christchurch), further study is needed on the influence of groundwater on these pollutant transformation processes, such as the physical effects of groundwater seepage on streambed condition and sediment resuspension, or chemical effects such as hardness contributed from groundwater.

Sediment

Coarser sediment is likely to settle out within the stormwater conveyance system in areas of low energy, such as sumps. This sediment is periodically removed from the system through sump cleaning and maintenance and therefore unlikely to enter the receiving waterway. However, finer sediment will likely be flushed through to the receiving waterway, where some will settle out over longer periods of time around low energy zones including adhering to instream vegetation.

Studies have shown that there is typically an inverse relationship between sediment size and particulate-bound copper and zinc concentrations (Sansalone & Buchberger 1997a; Herngren *et al.* 2006), meaning that a higher proportion of particulate copper and zinc is expected to reach the waterways as it is primarily attached to the finer, harder-to-settle sediment. It would be valuable to assess the fraction of metals proportion to particle size in runoff from different impermeable surfaces to further guide appropriate treatment selection. Additionally, less is known about the long-term transformation of these metals within the streambed sediments, i.e. whether fine fraction particulate metals are released in dissolved form in response to changing redox, pH and organic conditions as instream organic matter decomposes.

Metals

pH buffering, due the presence of alkalinity (as observed in this study's concrete tile roof and road surfaces), in the stormwater network and in the receiving waterway will transform dissolved metals into particulate form and accordingly reduce the associated ecotoxic effects and bioaccumulation rates of metals in aquatic life. Conversely, the increased flow and turbidity in the stream during wet weather conditions may resuspend stream bed sediment and its associated metals. The addition of modelling modules that consider pH buffering and physical mixing processes would enhance the power of the

MEDUSA model in predicting pollutant concentration and form throughout the stormwater network discharge points.

8.3.2 Expansion of characterised conditions: surface type, topography, climate, land use

While the model has been successfully applied to both the Okeover and Addington catchments (in the low intensity rainfall climate of Christchurch), further research is needed to characterise the relationship of pollutant load generation to a wider range of climatic, topographic and land use characteristics, such that the model performance can be assessed for its universality of application. Application of the model through untreated runoff sampling and recalibration should therefore be done outside of Christchurch; both elsewhere in New Zealand and overseas. Also, priorities for further runoff sampling and model application within the low intensity rainfall climate of Christchurch include: 1) one of the Heathcote subcatchments, due to its closer proximity to the Port Hills and potential increased atmospheric deposition of wind-blown loess soils (i.e. quantifying the influence of topography on individual surfaces' runoff quality), and 2) the Christchurch Central Business District (CBD), due to its density of impermeable surfaces and its significant changes and redevelopment post-earthquake.

8.3.3 Addition of other pollutants into model framework

The model provides a framework for incorporating other pollutants based on their relationship to rainfall characteristics. Other pollutants that could be added include other metals, hydrocarbons and nutrients. Metals could readily be incorporated based on the assumption that the same relationships apply as copper and zinc, but with metal-specific calibrated model coefficient values. The inclusion of hydrocarbon predictions would require an assessment of hydrocarbon build-up and wash-off relationships to rainfall characteristic and development of appropriate equations to represent these processes. Permeable surface areas would need to be included in the model to enable predictions of nutrient loads (contributed via runoff and soil erosion processes).

The PSD characterisation undertake in this research also identified some significant correlations between key PSD metrics, such as D_{50}, and rainfall variables. This suggests these rainfall variables could be used to predict PSD metrics within the model. This would allow not only sediment loads to be predicted for prioritizing surfaces to target for sediment removal but also guide the selection and design of treatment to most effectively remove sediment in runoff from the priority surfaces, based on the predicted PSD profile.

8.3.4 Optimal placement of treatment systems in a catchment

As well as appropriate treatment selection, research is needed on the optimal placement of treatment systems within a catchment to best suit the expected pollutant load character. MEDUSA can be used to explore the effect of implementing different treatment systems to suit the character of the runoff at any particular site, through addition of a load reduction factor or similar to represent implemented policies or treatment systems applied to targeted surfaces. The lack of quantification of stormwater treatment effectiveness poses a key barrier for successful implementation of stormwater improvements in established urban areas. The predicted effectiveness could be integrated within a decision support system with other factors such as costs and available land area to assist in the selection of an appropriate stormwater management approach.

8.3.5 Understanding climate change effects on pollutant generation

Modelling showed that overall contaminant generation was most sensitive to variation in rainfall intensity and duration. These two factors are key climate variables that are expected to change under projected climate change scenarios (on both a local, Christchurch scale as well as globally). Simulation using MEDUSA with potential climate change scenarios will help understand future trends of pollution loadings of urban streams.

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Appendix A Untreated runoff quality database

Table A1: National and international references used for comparison of untreated runoff quality

Region	Reference	Runoff type	Sample type [1]	Data scope	Reported parameters
New Zealand	(Williamson 1986)	Mixed (residential)	EMC	2 individual sites	TCu, TZn, TPb
	(Auckland Regional Council 1992a)	Mixed (industrial; residential)	EMC	2 individual sites	TCu, TZn, TPb
	(Leersnyder 1993)	Mixed (commercial)	EMC	1 individual site	TSS, TCu, TZn, TPb
	(Auckland Regional Council 1994)	Mixed (residential)	EMC	1 individual site	TCu, TZn, TPb
	(Mosley & Peake 2001)	Mixed (residential)	EMC	1 individual site	TZn
	(NIWA 2001)	Mixed (residential; commercial; industrial)	EMC	3 individual sites	TCu, TPb
	(Larcombe 2002)	Mixed (institutional)	EMC	1 individual site	TCu, TPb
	(Pennington 2004)	Mixed (residential; mixed commercial/industrial)	EMC	2 individual sites	TCu, TZn, TPb
	(Pennington 2004)	Roofs (Coloursteel® tile; concrete tile; decramastic tile; long run Coloursteel®)	EMC	4 individual sites	TZn
	(Pennington & Webster-Brown 2008)	Roofs (copper x3; concrete roof with copper guttering)	FF and SS	4 individual sites	TCu
	(Zollhoefer 2009)	Mixed (residential x2)	FF and EMC	2 individual sites	TSS, TCu, TPb
	(Auckland Regional Council 2010b)	Roads (low-moderate traffic density; motorway)	EMC	2 individual sites	TSS, TCu, TZn
	(Auckland Regional Council 2010b)	Roofs (galvanized unpainted; galvanized poor paint; galvanized well painted; decramastic; Zincalume® unpainted; concrete; copper; other non-metallic)	EMC	8 individual sites	TSS, TCu, TZn
	(Fassman & Blackbourn 2011)	Road (asphalt)	EMC	2 individual sites	TSS, Tcu, TZn, TPb
	(Trowsdale & Simcock 2011)	Road	EMC	1 individual site	TSS, Tcu, TZn, TPb
Combined	(Williamson 1993)	Mixed (unspecified land use)	EMC	Combined sites	TSS
	(Göbel *et al.* 2007)	Roofs (non-metallic; non-metallic with zinc guttering; green; copper; aluminium; zinc)	EMC	Combined sites	TSS, TCu, TZn, TPb
	(Göbel *et al.* 2007)	Roads (service road; main road; motorway)	EMC	Combined sites	TSS, TCu, TZn, TPb
	(Bratieres *et al.* 2008)	Mixed (unspecified land use)	EMC	Combined sites	TSS, TCu, TZn, TPb

Region	Reference	Runoff type	Sample type [1]	Data scope	Reported parameters
Asia	(Gan *et al.* 2008)	Road (unspecified traffic density)	EMC	1 individual site	TSS, TCu, TZn, TPb
	(Arora & Reddy 2014)	Mixed (unspecified land use)	EMC	1 individual site	TSS, TCu, TZn, TPb
	(Chow & Yusop 2014)	Mixed (residential; commercial; industrial)	EMC	3 individual sites	TSS, TZn
Europe	(Boller 1997)	Roofs (polyester; tile)	EMC	2 individual sites	TCu, TZn, TPb
	(Daligault *et al.* 1999)	Mixed (residential/institutional; residential)	EMC	2 individual sites	TSS, TCu, TZn, TPb
	(Zobrist *et al.* 2000)	Roofs (polyester; tile)	FF and SS	2 individual sites	TSS, TCu, TZn, TPb
	(Salvia-Castellvi *et al.* 2005)	Mixed (residential)	EMC	1 individual site	TSS, TCu, TZn, TPb
	(Rule *et al.* 2006)	Mixed (industrial; residential)	FF	2 individual sites	TCu, TZn, TPb
	(Boogaard & Lemmen 2007)	Mixed (unspecified land use)	EMC	Combined sites	TSS, TCu, TZn, TPb
	(Kafi *et al.* 2008)	Mixed (unspecified land use)	EMC	1 individual site	TSS, TCu, TZn, TPb
	(Schriewer *et al.* 2008)	Roof (zinc)	EMC	1 individual site	TZn
	(Farreny *et al.* 2011)	Roofs (clay tiles; metal sheet; polycarbonate plastic; flat gravel)	EMC	4 individual sites	TSS
Middle East	(Taebi & Droste 2004)	Mixed (unspecified land use)	EMC	Combined sites	TSS, TCu, TZn, TPb
North America	(Driscoll *et al.* 1990)	Urban roads	EMC	Combined sites	TSS, TCu, TZn, TPb
	(Novotny 1992)	Mixed (unspecified land use)	SMC	1 individual site	TSS
	(Good 1993)	Roofs (plywood with roof paper/tar; old metal roof with aluminium paint; aluminium roofs x 2)	EMC	4 individual sites	TCu, TZn, TPb
	(Bannerman *et al.* 1996)	Mixed (unspecified land use)	SMC	1 individual site	TSS
	(Smullen *et al.* 1999)	Mixed (compilation of sample data >20 years old)	EMC	Combined sites	TSS, TCu, TZn, TPb
	(Davis *et al.* 2001)	Roofs (residential; commercial; institutional)	EMC	3 individual sites	TCu, TZn, TPb
	(Macdonald 2003)	Mixed (unspecified land use)	SMC	1 individual site	TSS
	(Dean *et al.* 2005)	Highway runoff	EMC	1 individual site	TSS, TCu, TPb
	(McLeod *et al.* 2006)	Mixed (commerical; residential x 2)	SMC	3 individual sites	TSS
	(Carpenter & Kaluvakolanu 2010)	Roofs (asphalt; green; stone)	EMC	3 individual sites	TSS
	(Francey *et al.* 2010)	Mixed (compilation of sample data <20 years old)	EMC	Combined sites	TSS, TCu, TZn, TPb

Region	Reference	Runoff type	Sample type [1]	Data scope	Reported parameters
Oceania	(Bach *et al.* 2010)	Mixed (commercial; high density residential)	FF and SS	2 individual sites	TSS
	(Bach *et al.* 2010)	Roofs (treated aluminium)	FF and SS	1 individual site	TSS
	(Francey *et al.* 2010)	Mixed (commercial; high density residential)	EMC	2 individual sites	TSS, TCu, TZn, TPb
	(Francey *et al.* 2010)	Roof (treated aluminium)	EMC	1 individual site	TSS, TCu, TZn, TPb

[1] FF – first flush; SS – steady state; EMC – event mean concentration; SMC – site mean concentration.

Appendix B Stormwater-related planning and policy hierarchy for Christchurch

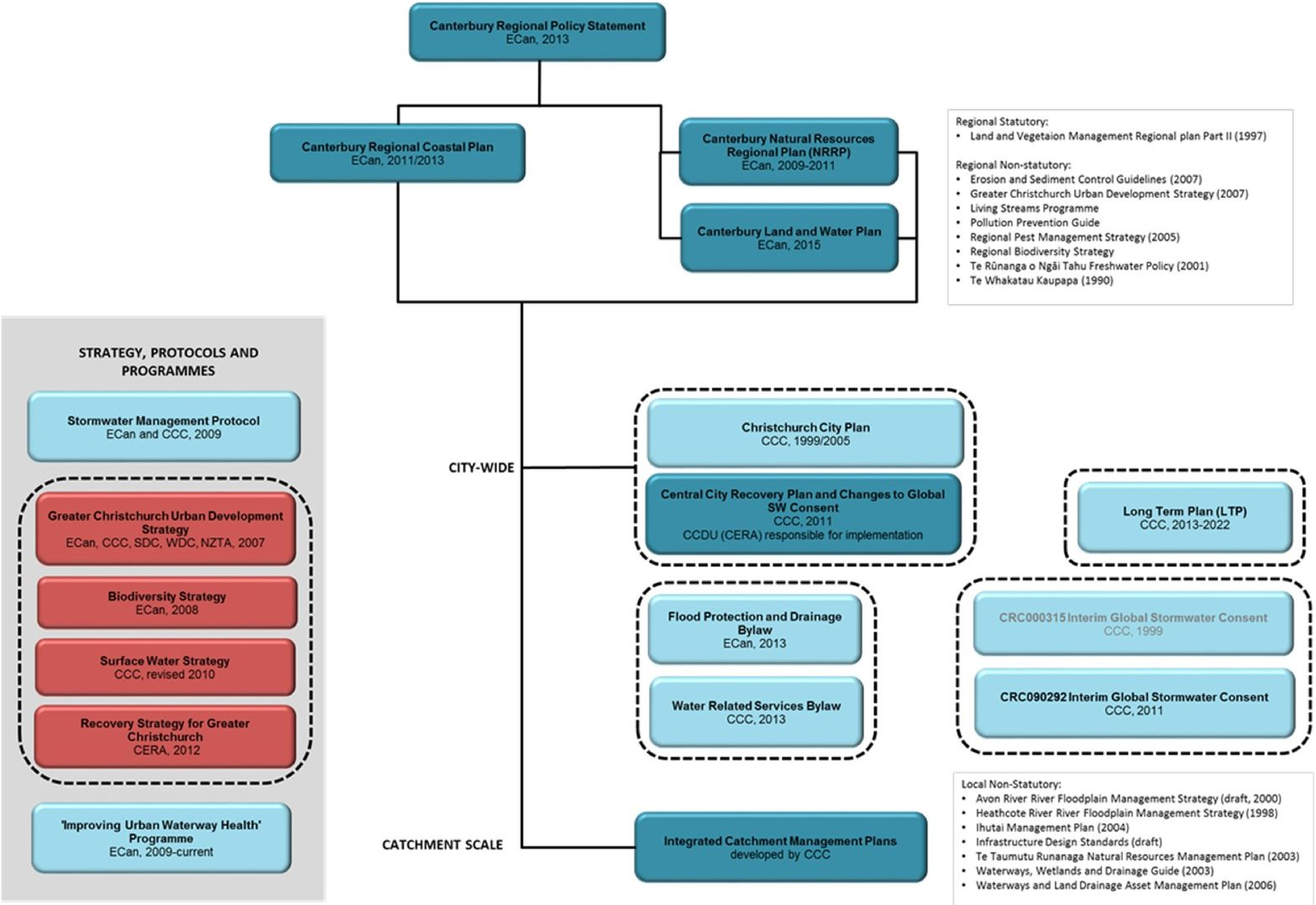

Figure B1: Hierarchy of planning and policy documents relevant to stormwater management in Christchurch

Appendix C Overview of stormwater management options

Table C1: Summary of infrastructure and source reduction options for improving stormwater (Digman *et al.* (2012), Christchurch City Council (2003))

		Treatment mechanism																		Main pollutants addressed								
Option	**Brief description**	**Reducing flow velocities**	**Allow sediment settling**	**Enhanced sedimentation**	**Extended detention**	**Flow retardation**	**Runoff volume reduction**	**Biological Uptake**	**Adsorbtion**	**Absorption**	**Coarse Filtration**	**Fine Filtration**	**UV disinfection**	**Overland flow**	**Evapotranspiration**	**Coalescence**	**Conveyance**	**pH buffering**	**Restricted Uptake**	**Coarse sediment**	**Fine sediment**	**Soluble particulates**	**Nitrogen**	**Heavy metals**	**Oil and grease**	**Hydrocarbons**	**Peak Flow**	**Volume**
Aquifer storage and recovery	Enhancing groundwater recharge via pumping or gravity feed of runoff. The quality of the runoff needs to be sufficient to protect the beneficial uses of the receiving groundwater.						X																					X
Bioretention basins	Same treatment functions as bioretention swales, except for conveyance. High flows are diverted away from structure or discharged into an overflow structure.		X		X	X		X	X			X									X	X	X					
Bioretention swales, biofiltration trenches	Bioretention systems located in base of swale. Fine media layer, with underdrain. Vegetation in media provides biofilms that enable adsorbtion.				X	X		X	X			X					X				X	X	X					
Buffer units	Buffer units provide a carbonate source as a buffering agent to control the pH of the runoff. This is particularly important for contaminants such as metals, where pH has a crucial role in whether they are in a dissolved or precipitated state. Typically would use a media such as limestone chips as the carbonate source.																	X						X				
Change in household chemical use	This could apply to activities such as: car washing and lawn and garden fertilising																		X		X	X	X					
Constructed wetlands	Shallow, extensively vegetated water bodies. Can have inlet zone for pre-treatment of coarse sediments. May have bypass to protect vegetated 'macrophyte zone' from high flows			X	X	X		X	X	X	X	X								X	X	X	X					
Downpipe disconnection	Instead of draining the downpipes from roofs into a stormwater pipe and conveying the runoff off the property, the downpipes can be disconnected from the stormwater pipe and instead discharge directly into a soakhole in the ground.						X																					X
Green roofs	The roof is covered with a waterproof membrane, media (typically a lightweight free-draining aggregate) and plants. Rain falling on the roof percolates down through the media to an underdrain system which collects the percolated water and conveys its downstream.					X	X	X			X	X			X					X	X	X	X				X	X
Infiltration trench	Trench or tank that collects runoff and then allows it to infiltrate into the surrounding soils.					X	X																					X
Oil/grit separators	Oil/grit separators capture coarse sediment and debris and separate oil from stormwater runoff, prior to the collected flow continuing downstream (e.g. it may be installed at a collection sump in a carpark area).										X					X				X					X			

Option	Brief description	Treatment mechanism																	Main pollutants addressed								
		Reducing flow velocities	Allow sediment settling	Enhanced sedimentation	Extended detention	Flow retardation	Runoff volume reduction	Biological Uptake	Adsorbtion	Absorption	Coarse Filtration	Fine Filtration	UV disinfection	Overland flow	Evapotranspiration	Coalescence	Conveyance	pH buffering	Restricted Uptake	Coarse sediment	Fine sediment	Soluble particulates	Nitrogen	Heavy metals	Oil and grease	Hydrocarbons	Peak Flow	Volume
Permeable surfaces	Constructed surfaces that are load-bearing while enabling surface water to infiltrate, as the material itself may be porous or there are voids and joints in the surface. The surface water may ultimately infiltrate to ground or to a sub-base and from there continue on downstream in the stormwater system.					X	X																				X	X
Ponds	Water body, well suited to steep topography. Requires pre-treatment for coarse sediments.		X						X				X								X							
Porous asphalt	Open graded asphalt (reduced sands and fines) allows for surface water to infiltrate to ground. It is generally recommended for low speed areas - footpath, carparks for example.						X				X									X							X	X
Proprietary on-site treatment systems	These units can be designed to target specific contaminants. Size, maintenance requirements and performance vary.																											
Rain gardens, bioinfiltration basins	A rain garden can function as either a bioretention basin that filtrates and collects via an underdrain to continue downstream, or as an infiltration basin where the collected runoff infiltrates to the surrounding soils.					X	X	X	X			X																
Rainwater tanks	A rainwater tank is used to collect runoff from roofs, either to detain the peak flow and release it into the pipes stormwater system at a slower rate (flow retardation), or to reuse the water onsite at a later time for irrigation (volume reduction).					X	X																				X	X
Roof material choice and maintenance	Selection of material controls what contaminants enter the runoff, as does maintenance (e.g. regular painting)																		X					X				
Sand filters	Operate similar to a bioretention system except have no vegetation growing on surface. Generally would have pre-treatment to remove coarse material. Stormwater percolates through sand media and is collected in underdrain and conveyed onwards. During high flows water can pond on the surface. Very high flows are diverted to protect the sand media from scour.				X	X			X			X					X				X	X						
Sediment basins: wet and dry basins	Retains coarse sediment (>=0.125mm). Used as pretreatment for elements such as wetlands. Important for protecting downstream elements from becoming overloaded or smothered with sediment. More typically used for construction sites runoff control.	X	X								X									X								
Swale or buffer systems	Used for conveyance in lieu of pipes. Usually operate best with a 2-4% slope. <2% require underdrains to avoid waterlogging, >4% require check dams to control flow velocity and distribute flows more evenly.	X										X		X			X			X								

Appendix D Supplementary untreated runoff quality analysis

In addition to TSS, copper, zinc, particle size distribution and total alkalinity, some additional data was collected on other water quality parameters as part of a basic screening process for pollutants of concern. This appendix outlines the lab analysis methodologies used and results from these screening analyses.

Methodology

Table D1 summarises the analytical methods used for each parameter, in accordance with the Standard Methods for Examination of Water and Wastewater jointly produced by the American Public Health Association (APHA), the American Water Works Association (AWWA) and the Water Environment Federation (WEF). Table D2 provides a summary of the number of samples tested for each analyte.

Table D1: Record of stormwater runoff quality analytical methods

Parameter	Units	APHA method	Brief description	Detection range
Total metals digestion (metals preparation)	N/A	3030 E	Boiling nitric acid. For preparation of metals for ICP-MS analysis.	--
Filtration (metals preparation)	N/A	3030 B	Sample filtration through 0.45 µm and preserved with nitric acid. For preparation of metals for ICP-MS analysis. Dissolved metals were filtered prior to preservation; total metals were filtered post-digestion.	--
Total metals	µg/L	3125 B	Method 3030 E, 3030 B, ICP-MS (trace level)	Various
Dissolved metals	µg/L	3125 B	Method 3030 B, ICP-MS (trace level)	Various
COD	mg/L	--	Digestion prior to colorimetric measurement	2-1,200 (high range) 3-150 (low range)
DRP	mg/L PO_4^{3-}	--	Ascorbic acid method	0-2.5
NH_4-N	mg/L	--	Salicylate method	0 – 2.5
Total Acidity	mg/L as $CaCO_3$	2310 B	Titrate 200 mL sample with 0.02 N NaOH to pH 8.3	> 1

Table D2: Record of samples screened for total ammonia, acidity, DRP and COD number of events (number of samples)

Surface	Pollutant			
	Total ammonia	COD	DRP	Acidity
Concrete roof	4 (18)	2 (12)	--	--
Copper roof	-	-	--	3 (9)
Galvanised roof	3 (13)	1 (6)	1 (3)	2 (2)
Asphalt road	3 (9)	2 (6)	--	--

Total acidity

The presence of acidity in the runoff may indicate increased corrosion of metallic surfaces (with associated increased heavy metal loads in the runoff). For total acidity, the titrant used was 0.02 N NaOH and the titrant was added until pH 8.3 was reached. Total alkalinity (mg/L as acidity) was calculated using as follows:

$$Total\ alkalinity = \frac{Vol_{titrant} * N * 50{,}000}{Volume\ of\ sample} \qquad \text{(D1)}$$

Chemical Oxygen Demand (COD)

COD is a measure of the amount of oxygen consumed per litre of solution, based on the oxidation of organic compounds to carbon dioxide under acidic conditions. It therefore is an indirect measure of the amount of organic compounds (i.e. both biologically available and inert organic matter) in the sample. The biologically available portion of organic matter is of interest in terms of potential environmental effects as it is degraded by oxygen-consuming bacteria under aerobic conditions. As fish and other aquatic organisms need dissolved oxygen in the water to survive, a high oxygen demand may signal loss of species diversity and die-off. However, measuring COD is a faster test than measuring the oxygen demand of the biologically available portion only (i.e. Biochemical Oxygen Demand (BOD)), and was considered most suitable for screening purposes undertaken for this research.

2 mL of sample was pipetted into 5 mL of COD digestion solution, and the mixture was boiled on a heating block at 150°C for 2 hours. Room temperature COD high range (20-1,200 mg/L COD) digestion solution was used. Where the results were below the detection limit for the high range method, some Hach-supplied low range (3-150 mg/L COD) digestion solution was used. Two quality control samples were done for each batch using a solution of known 600 mg/L COD concentration (as this is mid-range for the high range digestion solution detection limits) to confirm that the preparation of samples produced results within 5% of the known concentration. All COD analysed were completed within 48 hours of sample collection.

Total Ammonia

The term ‘ammonia’ refers to two chemical species of ammonia that are in equilibrium in water: the un-ionised ammonia, NH_3, and the ionised ammonium ion, NH_4^+. The proportion of the two chemical forms in water varies with the physico-chemical properties of the water, particularly pH and temperature. Ammonia is very soluble in water, and therefore is readily available for uptake by aquatic organisms (Taylor *et al.* 2005). Ammonia is associated with eutrophication, hypoxia and loss of biodiversity and habitat.

2 mL of sample was pipetted into Hach-manufactured Test’n’Tube vials pre-filled with 5 mL of Hach proprietary solution. Pre-filled ‘powder pillows’ of ammonia salicylate and ammonia cyanurate were each added to the mixture, before it was thoroughly shaken and left to react for 20 minutes. A method blank was prepared using the same process, but with 2 mL of deionised water as the ‘sample’ equivalent. The method blank was used to zero the Hach DR3900 Benchtop Spectrophotometer machine, prior to reading each vial. All total ammonia analyses were completed within 6 hours of sample collection.

Dissolved Reactive Phosphorus

Dissolved reactive phosphorus is a measure of the soluble phosphorus that is readily available for uptake by aquatic organisms. While it is naturally present at low levels in surface water and is essential for plant life, excess phosphorus causes eutrophication and resultant loss of biodiversity and habitat.

10 mL of sample was pipetted into Hach-manufactured sample cell. Pre-filled ‘PhosVer 3 phosphate powder pillows’ were each added to the sample cell, before it was thoroughly shaken and left to react for 2 minutes. A method blank was prepared using the same process, but with 10 mL of deionised water as the ‘sample’ equivalent. The method blank was used to zero the Hach DR3900 Benchtop Spectrophotometer machine, prior to reading each vial. All dissolved reactive phosphorus analyses were completed within 6 hours of sample collection.

Results and discussion

Other heavy metals

As aluminium (Al), arsenic (As), cadmium (Cd) and nickel (Ni) have also been observed to be present at elevated concentration in urban runoff (Zanders 2005; O'Sullivan & Taffs 2007), dissolved concentrations measured for the four metals were assessed against ANZECC guidelines (Figure D1). It should be noted that any runoff discharged into a receiving waterway will undergo transformational processes both during conveyance of the runoff from its original surface to the point of entry into the waterway, as well as mixing and dilution within the waterway. The partitioning of the metals into dissolved or particulate form will therefore change until it is fully mixed instream. Therefore the values of untreated runoff quality sampled at the source cannot be directly compared to the guideline values. Nevertheless, it is useful to undertake an indicative assessment to gauge whether there is potential for an exceedance in the guideline values. From this analysis of the four aforementioned metals, only dissolved Al in the road runoff showed concentrations within the interquartile range of results greater than the 95% Level of Protection values. As and Ni were observed to have few sample results above the 99% Level of Protection (i.e. most stringent) guideline value. Overall, the concentrations of these heavy metals do not indicate they are present at 'levels of concern' from the four sampled surfaces.

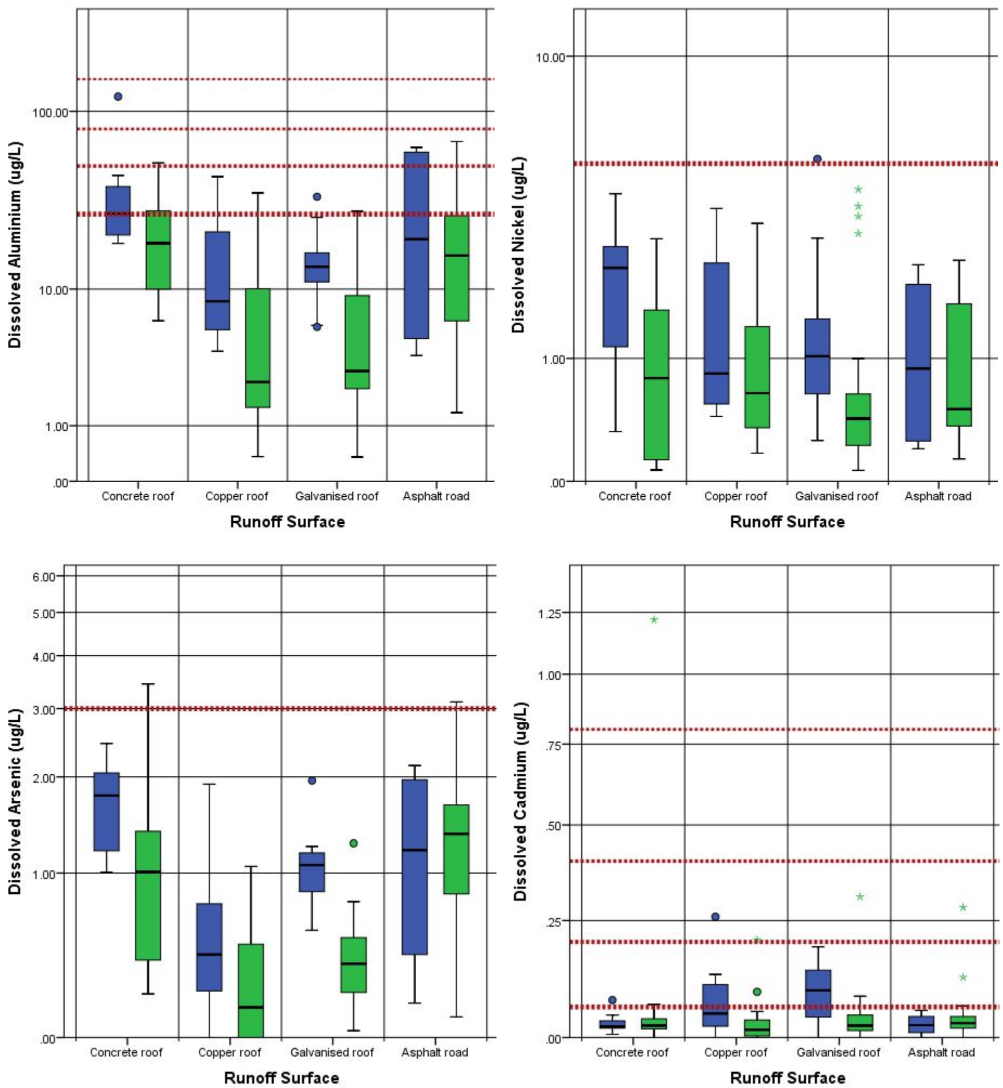

Figure D1: Dissolved Al, As, Cd and Ni concentrations against ANZECC guideline values

Total ammonia, Dissolved Reactive Phosphorus, Acidity, Chemical Oxygen Demand

Total ammonia samples were all below the ANZECC guideline value of 1.32 mg/L, with the sole exception of a first flush road sample (SF11 Rd_1) at 1.33 mg/L (Figure D2).The ANZECC guideline values are 0.44 mg/L for nitrate + nitrite-N. Given that the total ammonia concentrations were not elevated above guideline levels and would be expected to be transformed by lithoautotrophic bacteria (i.e. nitrification) to nitrite-N and ultimately nitrate-N, the contribution to nitrate and nitrite concentrations through the nitrification of ammonia would not be high. It was therefore decided to cease analysis of nitrogen forms for the remainder of the sampling programme.

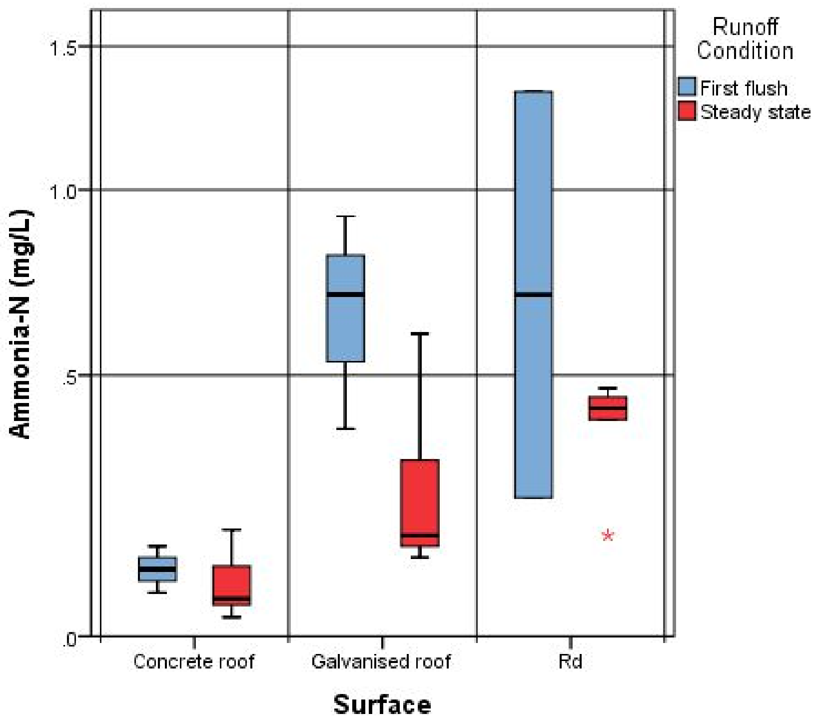

Figure D2: Total ammonia concentrations for select samples

COD for concrete roof samples ranged from <20 – 41 mg/L, with majority (9 of 12) of the samples being below the 20 mg/L limit of detection. All galvanised roof samples except one (at 22 mg/L) were below the 20 mg/L limit of detection. One event's road samples showed COD values of 223, 179 and <20 mg/L, where all samples were steady state samples, while the following event which included one first flush sample were all <20 mg/L. On the basis of the low COD concentrations seen in the concrete and galvanised roof samples and inconsistency seen in the road sample analyses, COD was discontinued from further analysis.

The acidity measured from the metallic roof runoff ranged between <2 mg/L and 6.6 mg/L. At these low concentrations, it was therefore decided to cease both COD and total acidity analysis.

Three galvanised roof samples were analysed for DRP with concentrations ranging from 0.4 - 2.4 mg/L. However, there were issues with the analytical procedure and instrumentation that could not be resolved and DRP analysis was discontinued.

Appendix E Duplicate samples values and Relative Percent Differences

Where the overall sample batch for a particular rain event was small, a duplicate may not have been taken for each sampled surface type. However, across all combined samples for each sampled event, a minimum of 1 duplicate for every 10 samples has been done. Tables E1 to E7 summarise the duplicate sample results and calculated Relative Percent Difference (RPD) for each pollutant and sampled surface.

Table E1: TSS sample values and Relative Percent Difference (RPD)

Surface	Event	Sample No.	Sample value	Duplicate sample value	Average value	RPD
Concrete roof	SF1	3	5.8	3.1	4.5	14.9%
	SF2	1	1.6	1.9	1.7	-3.8%
	SF3	3	0.8	0.8	0.8	1.1%
	SF4	1	1.8	2.3	2.1	-6.5%
	SF6	1	3.4	3.7	3.5	-1.9%
	SF7	1	6.0	4.3	5.1	8.3%
	SF8	1	58.5	22.7	40.6	22.1%
	SF9	3	2.5	1.9	2.2	6.1%
	SF11	1	7.7	7.0	7.4	2.5%
	SF12	5	0.1	0.1	0.1	0.0%
	SF17	4	8.2	7.0	7.6	4.2%
Copper roof	SF6	1	33.4	40.9	37.1	-5.0%
	SF8	2	55.5	27.3	41.4	17.0%
	SF9	2	24.2	9.3	16.7	22.3%
	SF10	3	36.4	42.7	39.5	-4.0%
	SF15	1	64.0	95.2	79.6	-9.8%
	SF17	2	2.6	1.1	1.9	20.0%
	SF18	2	6.5	7.9	7.2	-4.9%
	SF19	1	65.8	56.8	61.3	3.7%
Galvanised roof	SF2	4	0.9	0.5	0.7	13.6%
	SF3	2	11.1	7.1	9.1	11.0%
	SF4	2	5.3	4.9	5.1	2.0%
	SF6	1	6.2	7.5	6.9	-4.9%
	SF7	1	2.3	1.6	1.9	9.3%
	SF8	7	0.4	0.8	0.6	-16.7%
	SF9	1	17.5	16.2	16.9	1.9%
	SF11	2	13.3	15.1	14.2	-3.1%

Surface	Event	Sample No.	Sample value	Duplicate sample value	Average value	RPD
	SF12	5	1.1	1.5	1.3	-7.5%
	SF13	3	2.6	2.3	2.5	2.7%
	SF24	1	20.4	24.2	22.3	-4.3%
Asphalt road	SF3	2	16.1	16.5	16.3	-0.6%
	SF6	1	90.7	89.8	90.3	0.3%
	SF8	1	75.5	78.7	77.1	-1.0%
	SF9	2	5.6	9.0	7.3	-11.6%
	SF11	2	100.7	117.4	109.1	-3.8%
	SF15	1	94.1	38.8	66.5	20.8%
	SF17	2	32.4	33.6	33.0	-0.9%
	SF18	1	124.1	130.1	127.1	-1.2%
	SF19	1	318.9	335.9	327.4	-1.3%
	SF22	2	39.0	47.7	43.3	-5.0%
	SF23	1	27.6	28.3	27.9	-0.6%

Table E2: Total copper sample values and Relative Percent Difference (RPD)

Surface	Event	Sample No.	Sample value	Duplicate sample value	Average value	RPD
Concrete roof	2	1	13.1	13.2	13.1	-0.2%
	3	1	8.2	8.1	8.2	0.4%
	4	2	10.3	10.0	10.2	0.7%
	8	4	5.1	4.6	4.8	2.7%
	9	2	13.3	13.8	13.5	-0.8%
	11	4	5.9	6.4	6.1	-1.9%
	12	4	14.3	14.3	14.3	0.0%
	17	2	2.4	2.3	2.3	1.7%
Copper roof	5	1	1,623.4	1,621.7	1,622.5	0.0%
	6	1	414.9	430.1	422.5	-0.9%
	8	7	470.3	512.8	491.6	-2.2%
	9	7	743.0	750.4	746.7	-0.2%
	11	7	820.1	829.0	824.5	-0.3%
	17	5	1,199.5	1,099.7	1,149.6	2.2%
	19	1	1,721.9	1,471.7	1,596.8	3.9%
Galvanised roof	2	1	6.4	6.1	6.2	1.3%
	3	2	5.5	5.3	5.4	1.0%
	4	3	4.8	4.8	4.8	0.0%
	5	1	10.4	9.9	10.2	1.3%
	8	6	4.3	4.3	4.3	-0.4%
	9	1	8.9	9.2	9.0	-0.8%
	11	5	4.1	4.3	4.2	-1.0%
	12	1	11.9	12.3	12.1	-0.8%
	13	1	5.3	5.2	5.2	0.8%
	19	2	3.2	4.5	3.9	-8.3%
Asphalt road	3	2	12.3	13.0	12.7	-1.3%
	8	2	51.5	52.5	52.0	-0.5%
	9	2	7.5	8.0	7.7	-1.8%
	11	2	40.1	40.2	40.1	-0.1%
	15	1	45.3	44.4	44.8	0.5%
	17	1	9.6	10.1	9.9	-1.3%
	19	1	84.7	83.9	84.3	0.3%

Table E3: Total zinc sample values and Relative Percent Difference (RPD)

Surface	Event	Sample No.	Sample value	Duplicate sample value	Average value	RPD
Concrete roof	2	1	19.3	31.4	25.3	-12.0%
	3	1	8.3	10.1	9.2	-5.0%
	4	2	10.6	27.4	19.0	-22.2%
	8	4	12.2	7.3	9.8	12.6%
	9	2	24.0	27.6	25.8	-3.4%
	11	4	14.5	9.8	12.1	9.5%
	12	4	27.0	27.7	27.4	-0.6%
	17	2	41.0	5.0	23.0	39.1%
Copper roof	5	1	34.7	36.8	35.8	-1.4%
	6	1	25.3	36.4	30.8	-9.0%
	8	7	11.7	9.8	10.8	4.3%
	9	7	5.4	4.5	5.0	4.2%
	11	7	7.7	10.0	8.9	-6.7%
	17	5	18.7	23.6	21.2	-5.8%
	19	1	23.3	29.2	26.3	-5.7%
Galvanised roof	2	1	215.6	209.3	212.4	0.7%
	3	2	472.4	445.8	459.1	1.4%
	4	3	145.0	163.7	154.3	-3.0%
	5	1	1,160.9	1,163.9	1,162.4	-0.1%
	8	6	113.0	114.3	113.7	-0.3%
	9	1	670.5	681.0	675.8	-0.4%
	11	5	79.2	81.7	80.4	-0.8%
	12	1	845.8	848.2	847.0	-0.1%
	13	1	442.8	440.8	441.8	0.1%
	19	2	334.3	329.6	331.9	0.4%
Asphalt road	3	2	57.9	59.2	58.6	-0.6%
	8	2	201.1	204.9	203.0	-0.5%
	9	2	20.9	21.3	21.1	-0.5%
	11	2	160.8	157.0	158.9	0.6%
	15	1	155.2	154.4	154.8	0.1%
	17	1	74.9	60.0	67.5	5.5%
	19	1	439.1	418.0	428.6	1.2%

Table E4: Total lead sample values and Relative Percent Difference (RPD)

Surface	Event	Sample No.	Sample value	Duplicate sample value	Average value	RPD
Concrete roof	2	1	3.6	2.2	2.9	12.2%
	3	1	2.5	2.7	2.6	-1.1%
	4	2	2.1	2.1	2.1	-0.6%
	8	4	2.6	2.4	2.5	2.2%
	9	2	3.8	3.8	3.8	0.1%
	11	4	8.9	5.5	7.2	11.8%
	12	4	1.9	1.9	1.9	-0.8%
	17	2	2.9	2.0	2.4	8.9%
Copper roof	5	1	1.8	1.9	1.8	-1.5%
	6	1	7.7	8.0	7.9	-0.8%
	8	7	0.4	0.6	0.5	-10.6%
	9	7	0.4	0.3	0.4	6.9%
	11	7	1.3	0.7	1.0	15.1%
	17	5	0.9	0.9	0.9	1.9%
	19	1	2.1	3.5	2.8	-12.5%
Galvanised roof	2	1	1.0	0.9	0.9	1.5%
	3	2	1.3	1.2	1.2	3.0%
	4	3	0.5	0.5	0.5	-2.0%
	5	1	1.4	1.4	1.4	0.0%
	8	6	0.7	0.7	0.7	1.4%
	9	1	2.2	2.7	2.5	-5.1%
	11	5	0.5	0.5	0.5	-2.8%
	12	1	7.6	6.9	7.2	2.6%
	13	1	2.6	2.7	2.7	-0.5%
	19	2	0.5	0.6	0.5	-4.3%
Asphalt road	3	2	5.5	5.7	5.6	-1.2%
	8	2	31.7	32.1	31.9	-0.3%
	9	2	1.3	1.2	1.3	2.9%
	11	2	19.5	17.8	18.7	2.2%
	15	1	3.9	3.6	3.8	2.0%
	17	1	7.1	7.4	7.2	-1.1%
	19	1	44.3	46.6	45.4	-1.2%

Table E5: Dissolved copper sample values and Relative Percent Difference (RPD)

Surface	Event	Sample No.	Sample value	Duplicate sample value	Average value	RPD
Concrete roof	2	1	10.1	10.0	10.1	0.4%
	3	5	10.8	12.0	11.4	-2.5%
	4	3	5.0	5.7	5.4	-3.3%
	9	4	4.8	5.8	5.3	-5.0%
	17	3	1.6	1.7	1.6	-1.6%
	8	3	0.5	0.8	0.7	-11.1%
	11	1	11.5	11.4	11.4	0.2%
	12	3	4.0	3.8	3.9	1.2%
	18	1	3.6	4.5	4.0	-5.6%
	19	3	7.2	8.6	7.9	-4.4%
Copper roof	5	1	1,091.1	1,141.8	1,116.4	-1.1%
	6	1	119.5	120.3	119.9	-0.2%
	17	6	1,218.1	1,244.6	1,231.4	-0.5%
	8	1	653.2	629.8	641.5	0.9%
	9	6	529.0	528.8	528.9	0.0%
	11	3	2,650.9	2,698.3	2,674.6	-0.4%
Galvanised roof	2	2	0.5	0.6	0.5	-3.1%
	5	1	3.8	3.7	3.8	1.2%
	9	3	0.8	0.7	0.7	1.3%
	12	2	1.2	1.0	1.1	2.3%
	13	1	1.7	1.6	1.7	1.6%
	3	3	0.6	0.6	0.6	-0.4%
	4	1	2.6	2.6	2.6	0.0%
	11	2	2.8	2.8	2.8	0.0%
	8	5	1.9	1.9	1.9	0.0%
	6	1	0.3	0.3	0.3	3.6%
Asphalt road	15	2	11.2	13.6	12.4	-4.8%
	17	2	1.8	1.7	1.7	1.5%
	11	1	33.0	31.5	32.2	1.2%

Table E6: Dissolved zinc sample values and Relative Percent Difference (RPD)

Surface	Event	Sample No.	Sample value	Duplicate sample value	Average value	RPD
Concrete roof	2	1	17.1	18.1	17.6	-1.5%
	3	5	24.3	26.0	25.2	-1.7%
	4	3	12.4	13.1	12.8	-1.4%
	8	3	6.3	6.8	6.5	-1.8%
	9	4	13.3	14.0	13.6	-1.3%
	11	1	9.9	11.5	10.7	-3.6%
	12	3	8.7	8.6	8.6	0.3%
	17	3	8.3	13.9	11.1	-12.6%
	18	1	4.9	6.2	5.6	-6.1%
	19	3	9.3	9.3	9.3	0.0%
Copper roof	5	1	12.9	19.0	16.0	-9.5%
	6	1	7.8	7.1	7.4	2.6%
	8	1	24.5	27.6	26.0	-3.0%
	9	6	5.2	6.9	6.1	-6.8%
	11	3	61.2	55.2	58.2	2.6%
	17	6	15.7	16.1	15.9	-0.7%
Galvanised roof	2	2	179.0	181.9	180.5	-0.4%
	3	3	241.7	252.6	247.2	-1.1%
	4	1	1,273.3	1,329.9	1,301.6	-1.1%
	5	1	1,633.3	1,670.2	1,651.8	-0.6%
	6	1	112.6	105.3	109.0	1.7%
	8	5	178.6	184.0	181.3	-0.7%
	9	3	349.4	347.3	348.3	0.1%
	11	2	420.8	426.6	423.7	-0.3%
	12	2	357.0	366.6	361.8	-0.7%
	13	1	387.1	390.3	388.7	-0.2%
Asphalt road	11	1	102.3	94.6	98.4	2.0%
	15	2	67.1	70.7	68.9	-1.3%
	17	2	53.2	57.5	55.3	-1.9%

Table E7: Dissolved lead sample values and Relative Percent Difference (RPD)

Surface	Event	Sample No.	Sample value	Duplicate sample value	Average value	RPD
Concrete roof	2	1	1.3	1.3	1.3	0.2%
	3	5	3.5	4.0	3.7	-3.0%
	4	3	1.7	1.9	1.8	-2.9%
	8	3	0.2	0.2	0.2	-4.6%
	9	4	2.3	2.7	2.5	-4.2%
	11	1	1.0	1.0	1.0	-0.7%
	12	3	1.5	1.5	1.5	0.7%
	17	3	1.6	1.7	1.6	-1.6%
	18	1	0.8	1.3	1.0	-11.2%
	19	3	3.3	3.5	3.4	-1.6%
Copper roof	5	1	0.1	0.2	0.2	-9.2%
	6	1	0.1	0.1	0.1	2.3%
	8	1	0.1	0.1	0.1	1.6%
	9	6	0.2	0.2	0.2	-2.8%
	11	3	0.6	0.6	0.6	1.1%
	17	6	0.8	0.7	0.7	2.0%
Galvanised roof	2	2	0.1	0.1	0.1	-5.4%
	3	3	0.1	0.1	0.1	-2.6%
	4	1	0.5	0.6	0.5	-2.5%
	5	1	0.4	0.4	0.4	5.2%
	6	1	0.1	0.1	0.1	1.8%
	8	5	0.2	0.3	0.3	-8.0%
	9	3	0.1	0.1	0.1	-1.1%
	11	2	0.3	0.3	0.3	0.9%
	12	2	0.8	0.8	0.8	0.1%
	13	1	0.5	0.5	0.5	-1.8%
Asphalt road	11	1	1.3	1.3	1.3	-0.5%
	15	2	2.5	2.4	2.4	0.7%
	17	2	0.2	0.2	0.2	5.8%

Appendix F Datasets used for statistical analyses of TSS, heavy metals and PSD

Table F1: Datasets composition for statistical analyses in Chapter 4 (TSS and heavy metals)

Surface Type	Comparison of differences (Kruskal Wallis)		Comparison of FF to SS (Paired t-test)		Correlation of total to dissolved metals (Pearson's correlation)	Correlation of TSS to total metals (Pearson's correlation)
	No. of data points (TSS)	No. of data points (metals)	No. of pairs (TSS)	No. of pairs (metals)	No. of data points	No. of data points
Concrete roof	65	54	9	8	54	54
Copper roof	45	42	3	2	42	37
Galvanised roof	58	49	8	7	49	47
Asphalt road	38	27	5	4	27	26

Table F2: Dataset composition for statistical analysis in Chapter 5 (PSD)

Runoff Type	PSD Data			TSS Data *
	Intra-event variation (Paired t-test)	Differences between surfaces (Independent t-test)	Inter-event variation (Correlation analysis)	Differences between surfaces (Independent t-test)
	No. of pairs	No. of data points	No. of data points	No. of data points
Concrete roof	6	27	27	34
Copper roof	6	25	25	35
Galvanised roof	7	23	23	33
Asphalt road	6	28	28	31

* TSS data includes samples where insufficient volume could be collected for PSD analysis

Appendix G Year 2012 rainfall event characteristics

Table G1: Rainfall characteristics for the 88 events of year 2012

Date of event	Rainfall pH [1]	No. of antecedent dry days (days)	Rainfall intensity (mm/hr)	Event duration (hrs)
2-Jan-12	6.01	3	0.13	3
8-Jan-12	6.01	6	0.40	1
9-Jan-12	6.01	1	0.67	3
13-Jan-12	6.01	4	0.70	4
22-Jan-12	6.01	9	1.15	13
27-Jan-12	6.01	4	3.10	4
29-Jan-12	6.01	2	0.48	6
1-Feb-12	6.01	2	0.55	4
6-Feb-12	6.01	5	0.30	1
7-Feb-12	6.01	1	0.17	3
10-Feb-12	6.01	3	0.40	2
14-Feb-12	6.01	3	0.52	12
19-Feb-12	6.01	4	0.60	1
21-Feb-12	6.01	3	0.90	2
22-Feb-12	6.01	1	1.05	10
24-Feb-12	6.01	2	0.62	6
1-Mar-12	6.01	5	2.44	10
2-Mar-12	6.01	2	0.49	14
3-Mar-12	6.01	0.2	0.50	1
4-Mar-12	6.01	0.3	0.50	8
11-Mar-12	6.01	7	0.45	2
11-Mar-12	6.01	0.5	0.45	8
19-Mar-12	6.01	7	1.03	7
21-Mar-12	6.01	3	0.97	16
10-Apr-12	5.89	19	1.22	25
27-Apr-12	6.40	15	0.80	3
29-Apr-12	6.01	2	0.25	2
2-May-12	6.01	2	0.20	2
5-May-12	6.18	3	0.37	3
9-May-12	5.49	4	0.19	9
10-May-15	6.01	0.7	0.15	4
15-May-12	6.13	5	0.44	11
27-May-12	6.19	11	0.45	2
28-May-12	5.19	1	0.13	7
5-Jun-12	6.01	8	1.56	14
7-Jun-12	6.01	1	2.04	9
8-Jun-12	5.41	1	1.54	10
11-Jun-12	6.01	3	0.60	1
14-Jun-12	6.09	3	0.30	8
14-Jun-12	6.09	0.4	0.40	1
15-Jun-12	6.09	0.5	0.64	33

Date of event	Rainfall pH [1]	No. of antecedent dry days (days)	Rainfall intensity (mm/hr)	Event duration (hrs)
18-Jun-12	5.7	1	0.40	2
23-Jun-12	6.03	6	0.55	6
3-Jul-12	5.97	9	0.54	16
3-Jul-12	5.97	0.3	0.46	35
13-Jul-12	6.01	8	0.50	1
17-Jul-12	6.01	4	0.55	2
22-Jul-12	6.01	5	0.12	5
24-Jul-12	6.12	2	0.24	21
24-Jul-12	6.12	0.3	0.45	2
30-Jul-12	5.93	5	1.49	29
4-Aug-12	6.08	3	0.25	6
7-Aug-12	5.60	3	0.72	21
12-Aug-12	5.88	4	1.69	41
14-Aug-12	5.88	0.6	2.61	8
19-Aug-12	6.01	5	2.30	5
20-Aug-12	5.82	1	0.27	3
21-Aug-12	5.85	0.3	0.13	8
21-Aug-12	5.85	0.7	0.48	6
3-Sep-12	6.01	12	0.50	1
4-Sep-12	7.15	0.8	3.50	2
7-Sep-12	6.01	2	0.80	1
11-Sep-12	6.01	5	0.60	20
16-Sep-12	5.9	4	0.40	2
17-Sep-12	5.89	1	1.78	5
26-Sep-12	6.86	9	0.65	2
1-Oct-12	6.01	5	0.40	1
5-Oct-12	6.01	4	0.90	1
8-Oct-12	6.56	2	0.35	17
13-Oct-12	6.01	4	1.32	29
18-Oct-12	6.01	4	0.39	15
19-Oct-12	6.22	1	0.30	2
22-Oct-12	5.56	2	0.72	18
3-Nov-12	6.01	11	0.52	6
3-Nov-12	6.01	0.3	0.38	5
6-Nov-12	6.28	2	0.28	5
11-Nov-12	5.76	6	1.22	13
17-Nov-12	6.01	5	0.15	4
17-Nov-12	6.01	0.2	4.00	1
17-Nov-12	6.01	0.3	1.07	7
20-Nov-12	6.11	2	0.60	1
29-Nov-12	6.26	10	1.21	13
4-Dec-12	6.01	5	0.35	2
7-Dec-12	6.01	3	3.96	7
8-Dec-12	5.95	1	0.70	1

Date of event	Rainfall pH [1]	No. of antecedent dry days (days)	Rainfall intensity (mm/hr)	Event duration (hrs)
18-Dec-12	6.01	10	0.57	3
26-Dec-12	6.01	8	0.56	20
30-Dec-12	6.01	3	0.30	2

[1] Where rainfall pH was not measured for an event, the mean measured pH value has been taken as the rainfall pH for that event (mean pH = 6.01)

Appendix H Comparison of literature-derived and Okeover-calibrated MEDUSA coefficient values

Table H1: Summary of MEDUSA roof coefficient values

Coefficient	Description	Literature-derived			Okeover-calibrated		
		All roofs	New roofs	Old roofs	Concrete roof	Copper roof	Galvanised roof
TSS	*(Eqn. 6-4)*						
a_1	Build-up coefficient	0.430			0.6	2.5	0.4
a_2	Build-up coefficient	0.266			0.25	0.95	0.5
a_3	Capacity factor coefficient for wash-off	0.008			--	--	--
a_3	Capacity factor coefficient for wash-off	0.59			--	--	--
a_3	Capacity factor coefficient for wash-off	0.0036			--	--	--
a_3	Capacity factor coefficient for wash-off	0.59			--	--	--
k	Wash-off coefficient	9.33×10^{-3}			9.33×10^{-3}	9.33×10^{-3}	9.33×10^{-3}
Total Copper	***(Eqns. 6-14 to 6-17)***		*(Copper roof only)*				
b_1	Initial Cu concentration pH coefficient		53.65	197.43	2	100	2
b_2	Initial Cu concentration pH coefficient		-2.800	-3.325	-2.8	-2.8	-2.8
b_3	Initial Cu concentration ADD coefficient		1.3722	1.3722	0.5	1.372	0.5
b_4	Initial Cu concentration ADD coefficient		0.217	0.217	0.217	0.217	0.217
b_5	Initial Cu concentration intensity coefficient		2.5514	3.5672	3.57	3.57	3.57
b_6	Initial Cu concentration intensity coefficient		-0.238	-0.09	-0.09	-1	-0.09
b_7	Stationary Cu concentration pH coefficient		170.33	281.33	7	275	7
b_8	Stationary Cu concentration pH coefficient		-3.619	-3.732	-3.73	-3.3	-3.73

Coefficient	Description	Literature-derived			Okeover-calibrated		
		All roofs	New roofs	Old roofs	Concrete roof	Copper roof	Galvanised roof
Total Zinc	*(Eqns. 6-18 to 6-21)*		*(Zinc-based roof only)*				
c_1	Initial Zn concentration pH coefficient		-0.39	-0.26	-0.1	-0.1	-0.5
c_2	Initial Zn concentration pH coefficient		4.40	2.76	2	2	4
c_3	Initial Zn concentration ADD coefficient		0.9948	0.9948	0.1	0.1	0.2
c_4	Initial Zn concentration ADD coefficient		0.0535	0.0535	0.01	0.01	0.09
c_5	Initial Zn concentration intensity coefficient		2.5514	3.5672	1	0.8	1.5
c_6	Initial Zn concentration intensity coefficient		-0.238	-0.09	-3.1	-1.3	-2
c_7	Stationary Zn concentration pH coefficient		-0.266	-0.460	-0.007	-0.007	-0.23
c_8	Stationary Zn concentration pH coefficient		2.12	4.14	0.056	0.056	2.122
Dissolved Copper (Eqn. 6-26)			***(Copper roof only)***				
l_1	Proportionality coefficient of DissCu to TCu		0.78	0.78	0.46	0.77	0.28
Dissolved Zinc (Eqn. 6-27)			***(Zinc-based roof only)***				
m_1	Proportionality coefficient of DissZn to TZn		0.92	0.99	0.67	0.72	0.43
Shared across metals (Eqns. 6-16 to 6-17, 6-20 to 6-21)							
Z	Transition time from initial to stationary state	1.00			0.75	0.75	0.75

Table H2: Summary of MEDUSA road/carpark coefficient values

Coefficient	Description	Literature-derived	Okeover-calibrated
		All roads/carparks	All roads/carparks
TSS	*(Eqn. 6-6)*		
a_1	Build-up coefficient	0.430	2.9
a_2	Build-up coefficient	0.266	0.16
a_7	Capacity factor coefficient for wash-off	0.0125	--
a_8	Capacity factor coefficient for wash-off	0.0125	--
a_9	Capacity factor coefficient for wash-off	-0.625	--
k	Wash-off coefficient	8.0×10^{-4}	8.0×10^{-4}
Total Copper	***(Eqns. 6-22 and 6-24)***		
g_1/i_1	Proportionality coefficient of TCu to TSS	0.0015	4.41×10^{-4}
Total Zinc	*(Eqns. 6-23 and 6-25)*		
h_1/j_1	Proportionality coefficient of TZn to TSS	0.0023	1.96×10^{-3}
Dissolved Copper (Eqn. 6-26)			
l_1	Proportionality coefficient of DissCu to TCu	0.30	0.28
Dissolved Zinc (Eqn. 6-27)			
m_1	Proportionality coefficient of DissZn to TZn	0.28	0.43

Appendix I Comparison of Okeover- and Addington-calibrated MEDUSA coefficient values

Table I1: Comparison of optimised MEDUSA model coefficient values for Okeover (shaded) and Addington catchment

Surface[1]	TSS Coefficients (Chapter 6: Eqns. 6-4 and 6-6)		
	a_1	a_2	k
Concrete tile roof (Okeover: Cr)	0.6	0.25	9.33×10^{-3}
Copper roof (Okeover: Cu)	2.5	0.95	9.33×10^{-3}
Galvanised painted (Okeover: Gv)	0.4	0.5	9.33×10^{-3}
Galvanised roof moderate (Addington: TJD)	2.38	0.46	9.33×10^{-3}
Galvanised roof old (Addington: GBD)	1.82	0.50	9.33×10^{-3}
Major arterial road (Addington: PCR)	282	0.34	9.33×10^{-3}
Minor arterial road (Addington: LNR)	216	0.17	8.0×10^{-4}
Collector road (Okeover: Rd)	2.9	0.16	8.0×10^{-4}
Commercial carpark (Addington: TJC)	190	0.28	8.0×10^{-4}
Industrial carpark standard (Addington: KRC)	396	0.21	8.0×10^{-4}
Industrial carpark manoeuvring (Addington: GBC)	319	0.19	8.0×10^{-4}

Surface	TCu Coefficients (Eqns. 6-14 to 6-17, 6-22)										
	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	Z	g_1	i_1
Concrete tile roof (Okeover: Cr)	2	-2.8	0.5	0.217	3.57	-0.09	7	-3.73	0.75		
Copper roof (Okeover: Cu)	100	-2.8	1.372	0.217	3.57	-1	275	-3.3	0.75		
Galvanised painted (Okeover: Gv)	2	-2.8	0.5	0.217	3.57	-0.09	7	-3.73	0.75		
Galvanised roof moderate (Addington: TJD)	2	-2	0.4	0.37	2.8	-0.09	13.5	-3.732	0.75		
Galvanised roof old (Addington: GBD)	0.8	-2.8	0.55	1	2.1	-0.0001	4.6	-3.732	0.75		
Major arterial road (Addington: PCR)										0.440	
Minor arterial road (Addington: LNR)										0.810	
Collector road (Okeover: Rd)										0.441	
Commercial carpark (Addington: TJC)											0.458
Industrial carpark standard (Addington: KRC)											0.254
Industrial carpark manoeuvring (Addington: GBC)											0.615

Surface	TZn Coefficients (Eqns. 6-18 to 6-21, 6-23)										
	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	Z	h_1	j_1
Concrete tile roof (Okeover: Cr)	-0.1	2	0.1	0.01	1	-3.1	-0.007	0.056	0.75		
Copper roof (Okeover: Cu)	-0.1	2	0.1	0.01	0.8	-1.3	-0.007	0.056	0.75		
Galvanised painted (Okeover: Gv)	-0.5	4	0.2	0.09	1.5	-2	-0.23	2.122	0.75		
Galvanised roof moderate (Addington: TJD)	22	4	0.2	0.09	0.64	-2	-0.17	2.122	0.75		
Galvanised roof old (Addington: GBD)	625	2	0.14	0.11	0.61	-2	-0.03	3.2	0.75		
Major arterial road (Addington: PCR)										7.990	
Minor arterial road (Addington: LNR)										7.250	
Collector road (Okeover: Rd)										1.96	
Commercial carpark (Addington: TJC)											3.750
Industrial carpark standard (Addington: KRC)											4.450
Industrial carpark manoeuvring (Addington: GBC)											2.50

Surface	DCu Coefficients (Chapter 6: Eqn. 6-26)
	l_1
Concrete tile roof (Okeover: Cr)	0.46
Copper roof (Okeover: Cu)	0.77
Galvanised painted (Okeover: Gv)	0.28
Galvanised roof moderate (Addington: TJD)	0.23
Galvanised roof old (Addington: GBD)	0.20
Major arterial road (Addington: PCR)	0.33
Minor arterial road (Addington: LNR)	0.38
Collector road (Okeover: Rd)	0.28
Commercial carpark (Addington: TJC)	0.46
Industrial carpark standard (Addington: KRC)	0.22
Industrial carpark manoeuvring (Addington: GBC)	0.52

Surface	DZn Coefficients (Chapter 6: Eqn. 6-27)
	m_1
Concrete tile roof (Okeover: Cr)	0.67
Copper roof (Okeover: Cu)	0.72
Galvanised painted (Okeover: Gv)	0.43
Galvanised roof moderate (Addington: TJD)	1.00
Galvanised roof old (Addington: GBD)	0.85
Major arterial road (Addington: PCR)	0.59
Minor arterial road (Addington: LNR)	0.64
Collector road (Okeover: Rd)	0.43
Commercial carpark (Addington: TJC)	0.52
Industrial carpark standard (Addington: KRC)	0.29
Industrial carpark manoeuvring (Addington: GBC)	0.56